TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

INSTITUTE OF METALS DIVISION

1929

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vol. 83
N/C

PAPERS PRESENTED BEFORE THE DIVISION, AT PHILADELPHIA, OCT. 9–11, 1928, AND NEW YORK, FEB. 20–21, 1929

American Institute of Mining, Metallurgical, and Petroleum Engineers

NEW YORK, N. Y.
PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY
29 WEST 39TH STREET
1929

Notice

This volume is the third of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with non-ferrous metals and includes all papers presented at the Philadelphia Meeting, Oct. 9–11, 1928, and the New York Meeting, Feb. 20–21, 1929.

The series is a continuation of the previous publications and proceedings of the Institute of Metals Division. The complete list of publications and proceedings follows:

1908–1911 *Transactions* of the American Brass Founders' Association.

1912–1916 *Transactions* of the American Institute of Metals.

1917 *Journal* of the American Institute of Metals.

1918–1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes Nos. 60, 64, 69, 70, 71 and 73.

1927 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

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1929 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Institute of Metals Division.

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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

CONTENTS

PAGE

Officers and Committees 5

PAPERS

Passivity of Metals and Its Relation to Problems of Corrosion (Annual Lecture). By Ulick R. Evans 7

Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions. By G. D. Bengough, J. M. Stuart and A. R. Lee 29

Some Aspects of Corrosion Fatigue. By T. S. Fuller (With Discussion) 47

Corrosion of Metals as Affected by Stress, Time, and Number of Cycles. By D. J. McAdam, Jr. (With Discussion) 56

Corrosion of Tin and Its Alloys. By C. L. Mantell (With Discussion) 111

Some New Developments in Acid-resistant Alloys. By Burnham E. Field (With Discussion) 149

Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids. By H. A. Bedworth (With Discussion) 160

Practical Application of Corrosion Tests; Resistance of Nickel and Monel Metal to Corrosion by Milk. By Robert J. McKay, O. B. J. Fraser and H. E. Searle (With Discussion) 175

Correlation of Laboratory Corrosion Tests with Service: Weather-exposure Tests of Sheet Duralumin. By Henry S. Rawdon (With Discussion) 220

Inhibition of Corrosion of Aluminum by Soaps. By H. V. Churchill (With Discussion) 244

Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids. By Norman B. Pilling and Donald E. Ackerman (With Discussion) 248

Corrosion of Metals in the Lehigh Valley. By C. E. Reinhard (With Discussion) 280

Smoothing and Etching Cupronickel, Bronze, Brass and Steel. By H. B. Pulsifer (With Discussion) 291

Treatment and Structure of Magnesium Alloys. By John A. Gann 309

Stability of Aluminum and Magnesium Casting Alloys. By A. J. Lyon (With Discussion) 333

Equilibrium Relations in Aluminum-magnesium Alloys of High Purity. By E. H. Dix, Jr. and F. Keller (With Discussion) 351

Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal. By B. Egeberg and H. B. Smith (With Discussion) 373

High-strength Gold Alloys for Jewelry and Age-hardening Phenomena in Gold Alloys. By E. M. Wise (With Discussion) 384

Dispersion Hardening in Copper-base and Silver-base Alloys. By J. L. Gregg . 409

The Constitution of the Copper-silicon System. By Cyril Stanley Smith (With Discussion) 414

Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. By O. W. Ellis (With Discussion) 443

Gases in a Sample of Overpoled Fire-refined Copper. By O. W. Ellis (With Discussion) 470

Incipient Shrinkage in Some Non-ferrous Alloys. By J. W. Bolton and S. A. Weigand (With Discussion) 475

PAGE

Some Observations in Heat Treatment of Muntz Metal. By L. Russell van Wert (With Discussion) 498

High-strength Brasses. By O. W. Ellis (With Discussion) 508

Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys Containing Nickel and Silicon. By W. C. Ellis and Earle E. Schumacher (With Discussion) 535

Diffusion of Zinc into Copper. By Samuel L. Hoyt (With Discussion) 552

Some Practical Aspects of Creep in Zinc. By W. M. Peirce and E. A. Anderson 560

Effect of Arsenic on Dispersion-hardenable Lead-antimony Alloys. By K. S. Seljesater 573

A. Metallographic Study of Tungsten Carbide Alloys. By J. L. Gregg and C. W. Küttner (With Discussion) 581

Grain Growth in Metals Caused by Diffusion. Discussion by Axel Hultgren of paper by Floyd C. Kelley (*Proc.* Inst. Metals Div., 1928) 591

INDEX 595

A. I. M. E. OFFICERS AND DIRECTORS

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The Passivity of Metals, and Its Relation to Problems of Corrosion

By Ulick R. Evans,* Cambridge, England

(Institute of Metals Division Lecture,† 1929)

I should like to commence by saying how much I appreciate the honor which the American Institute of Mining and Metallurgical Engineers has done me in inviting me to visit your country, and to deliver this lecture before you. In choosing a subject, and in deciding what to include and what to omit, I have endeavored to discuss as far as possible work carried out recently in Europe with which you may not be unduly familiar. It would be poor return for your hospitality, and a mistaken sort of compliment indeed, if I were to load the lecture with accounts of researches carried out in your own country—researches with which you are probably better acquainted than I. Not that I have in any way excluded work done on this side of the Atlantic from my survey; one would indeed find it difficult to write on this, or on any other branch of science, without mentioning American work. But I have endeavored as far as possible to concentrate on aspects of the case which will, I hope, be comparatively fresh to you, and I feel fairly certain that this will be in accordance with your own wishes.

Films Produced at Elevated Temperatures

If a strip of iron is heated strongly at one end, the other end remaining cold, there is produced over the heated portion a layer of oxide scale, the thickness of which diminishes steadily with the distance from the hot end. Somewhere in the middle of the strip, the thickness of the oxidized layer will become comparable to the wave length of light, and over this region the thin films give rise to a series of beautiful interference tints, commonly known as "temper colors." The colors are caused by the fact that two trains of light waves are reflected respectively from the outer and inner surfaces of the oxide film, and the possibility arises that the "crests" of one series of waves may coincide with the "troughs" of the other, thus diminishing the intensity of the light of some particular wave length. The state of affairs in this part of the strip is shown diagrammatically in Fig. 1, in which the film thickness is enormously exaggerated, of course, in comparison with the length of the strip; the

* Cambridge University.

† New York Meeting, February, 1929.

values for the thickness of the film are based on recent determinations carried out by Constable[1] at Cambridge University.

At a thickness[2] of about 720 Å, the relatively long yellow waves suffer interference in the manner indicated, and the resultant light has a blue color, blue being complementary to yellow. A little further from the hot end, where the thickness is only about 580 Å, the rather shorter green waves are subdued, and the metal has a brown-red appearance; still further along the strip, at a thickness of about 460 Å, the short blue rays are extinguished, and the metal has a straw-yellow color. Below a thickness of about 400 Å, no colors are produced, since

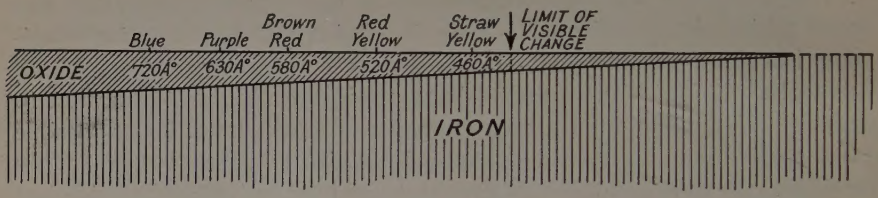

Fig. 1.

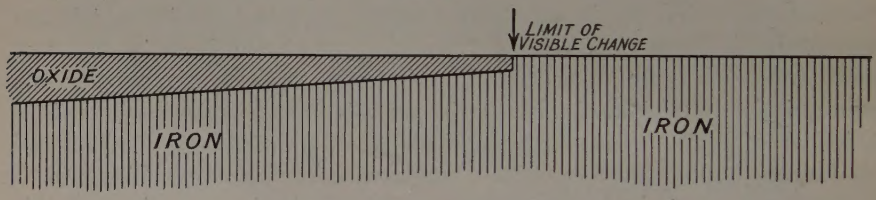

Fig. 2.

Figs. 1 and 2.—Diagrams of varying conditions in iron strips.

films thinner than this value could only produce interference of wave lengths too short to affect our eyes. Beyond the straw-yellow region, therefore, the iron appears silvery gray, and unchanged (Fig. 1). Nevertheless it seems logical to suppose that the film actually continues further, becoming thinner and thinner as the cold end is approached. A film of transparent matter too thin to produce interference tints would not necessarily be visible, so long as it is in optical contact with the bright metal; it should, however, become visible, if separated from the highly reflecting basis. There are some people who will never believe in the existence of anything which is not visible to the eye; these people, no doubt, would prefer to consider that the film suddenly terminates at just that thickness below which our eyes cease to be competent to follow it, an idea graphically represented in Fig. 2. Such a coincidence would appear unlikely; it seems much more probable that the film continues

[1] F. H. Constable: Spectrophometric Observations on the Growth of Oxide Films on Iron, Nickel, and Copper. *Proc.* Roy. Soc. (1928) **117A**, 376.

[2] Å is equal to 10^{-8} cm.

below the thickness of 400 Å, as suggested in Fig. 1, although at these lower thicknesses it is invisible.

Strong support of the idea of the invisible film is obtained if different parts of the strip are tested with drops of copper nitrate solution.[3] As is well known, copper nitrate solution acts on freshly abraded iron, giving metallic copper and iron nitrate. If a strip of pure electrolytic iron, freshly abraded, is heated at one end in the manner described, and if, after the whole has cooled down, drops of dilute copper nitrate solution are placed at the unheated end, metallic copper is quickly and copiously deposited. If, however, drops of the solution are placed at other points further along the strip, it will be found that the deposition of copper becomes slower and less copious, as the distance from the cold end increases. Before the tinted region is reached, a place is found where the drops produce no deposition of metallic copper at all; although at this place the iron is not *visibly* distinguishable from that at the cold end, yet its behavior towards copper nitrate is utterly different. It is interesting to note that soon after the visible region is entered, deposition of copper recommences, but it occurs at scattered points evidently representing cracks in the film.

The conclusion is almost irresistible. The oxide film is capable of protecting the iron from the attack of copper nitrate, provided that it is continuous and uncracked. Thick protective layers are especially liable to cracking, as is well known (thickly galvanized iron, for instance, is more likely to develop fissures in the zinc coat than thinly galvanized iron). Therefore it is not surprising to find that the thick visible scale shows deposition of copper locally; sometimes the cracks which permit it can actually be seen under the microscope. In the "invisible region," the film is thinner, less likely to crack, and consequently more perfectly protective. Still nearer the unheated end, however, the film becomes discontinuous, and copper deposition can occur, becoming more rapid and more profuse as the cold end is approached.

Films Produced at Ordinary Temperatures

The experiment just described proves that a short exposure to air at a slightly *elevated* temperature renders electrolytic iron unaffected by copper nitrate, but that a similar short exposure to air at *ordinary* temperatures still permits the iron to deposit copper. The question arises, would a long exposure to dry air at ordinary temperatures confer immunity? In the case of pure electrolytic iron, it is actually found that after long exposure to dry air the power to precipitate copper from copper nitrate solution is lost. We may speak of iron which deposits copper as being "active towards copper nitrate" and that which deposits no copper as being "passive towards copper nitrate." The passage

[3] U. R. Evans: Oxidation, Passivity and Corrosion. *Nature* (1926) **118**, 51.

from the active state to the passive state is a gradual one; the copper is deposited more slowly and less profusely as the period of exposure to air is increased; finally no copper is deposited at all. The time required to produce passivity varies from a few minutes, in the case of iron abraded with very fine emery, to several hours in the case of iron abraded with very coarse emery. Apparently the stresses left by grinding keep cracking the film, but the rents are repaired by fresh oxidation of the metal exposed at the fissures, and finally (after a period which depends on the violence of the original abrasion) the internal stresses become too much exhausted to produce further cracking, and the metal becomes passive. Specimens of pure iron rendered passive by exposure to air have been kept in M/20 copper nitrate for a year without change.

It should be noted, however, that metal which is passive towards copper nitrate is not necessarily passive to copper chloride or even to copper sulfate. Probably chlorine ions can penetrate weak points in the armor which the nitrate ions cannot pierce. But this is probably not the only factor at work. Copper nitrate is itself a mild oxidizing agent, and it seems likely that it can effect repairs to very minor flaws in the film, although if considerable discontinuities are present, or considerable stresses, copper deposition commences at once, and the healing of the film cannot occur. Furthermore, it should be noticed that although pure electrolytic iron can be rendered passive to copper nitrate merely by dry air, steel cannot with certainty be rendered passive in that way. It can, however, be rendered passive in other ways, for instance by immersion in potassium chromate solution, although the passivity is less persistent than that produced on pure iron, and deposition of copper usually occurs sooner or later. It is probable that the boundaries of the iron and carbide particles constitute weak points; there is good reason to believe that phase junctions are particularly liable to prove vulnerable places in a protective layer.

There are, of course, many other ways in which iron displays passivity. The behavior of iron towards concentrated nitric acid has always attracted special interest, largely because of the fascinating series of letters which passed between Faraday and Schoenbein on this subject about 92 years ago. Dilute nitric acid, as is well known, attacks iron with extraordinary rapidity; concentrated nitric acid has normally no action, the iron remaining apparently unchanged, so long as it is below the surface of the acid; nitric acid of intermediate concentrations often causes rhythmic alternation between the active (dissolving) and passive (undissolving) states. But nitric acid is not a very satisfactory reagent for obtaining passive iron; if a piece of pure iron is dipped into concentrated nitric acid, no reaction occurs; but if it is then removed, and allowed to drain, violent reaction often commences after a few seconds at the margin of the wetted area, and spreads over the whole

wetted surface; the fact that the breakdown occurs at the junction of three phases (iron, acid and air) should be noticed in passing.

It has been objected that the passivity of iron towards nitric acid cannot be due to an oxide film, since any oxide, it is alleged, would be dissolved by the acid. This objection has been entirely disposed of by a delightful piece of research carried out at Bedford College, London, by Hedges,[4] who showed that—in point of fact—ferric oxide (if freshly ignited and therefore free from hydroxide) is not dissolved by concentrated nitric acid at ordinary temperatures; on raising the temperature, the dissolution first becomes appreciable at just the temperature at which metallic iron begins to be attacked by nitric acid of the concentration in question. This points to the fact that the invisible film which normally protects iron from nitric acid is ferric oxide.

Another method of rendering iron passive depends on anodic treatment. At low current densities, an iron anode placed in, say, sodium sulfate solution dissolves smoothly as ferrous sulfate; if, in the desire to increase the rate of attack, the current density is raised, the contrary result is obtained, and, after a few minutes, the iron almost ceases to dissolve, the current being expended merely on the production of oxygen gas; there is, however, still a slow dissolution of iron, and it is interesting to note that this occurs, on a half-immersed anode, mainly at the water line; once more it is to be observed that breakdown occurs at the place where three phases (metal, air and solution) meet. It may also be remarked that while low current densities allow the iron anode to dissolve, and high current densities lead, in general, to passivity, intermediate current densities sometimes permit a rhythmic fluctuation between the active and passive conditions.[5]

The current density needed to produce passivity on an iron anode varies with the nature of the solution. In nitrate solutions where the anions have a distinctly oxidizing character, a low current density suffices; in chloride solution it is difficult to produce passivity at all—no doubt another instance of the power of the small, mobile chlorine ions to penetrate and undermine protective films. In alkaline solutions, where the discharge of $(OH)'$ ions would tend to convert the surface layer of the metal to insoluble oxide or hydroxide, passivity appears readily; in acid solutions, a high current density must be applied before passivity sets in.

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[4] E. S. Hedges: *Jnl.* Chem. Soc. (Pt. I, 1928) 969.

[5] This "periodicity" has recently been the subject of detailed investigation by E. S. Hedges: Periodic Phenomena at Anodes of Copper and Silver. *Jnl.* Chem. Soc. (Pt. II, 1926) 1533.

Periodic Phenomena at Anodes of Magnesium, Zinc, Cadmium, Mercury, Tin and Lead, and at an Unattackable Anode. *Idem*, 2580.

Periodic Electrochemical Passivity of Iron, Cobalt, Nickel and Aluminium. *Idem*, 2878.

Here again, the fact that passivity can be produced at all in acid solution has caused some investigators to doubt whether the phenomenon could be ascribed to an oxide film; surely, it was argued, the acid would dissolve away any oxide present? Recent investigations, however, seem to suggest that at the moment when passivity actually sets in, the layer of liquid next to the metal has ceased to be capable of dissolving iron oxide; on the contrary, it is already supersaturated with some solid body (sulfate, basic sulfate or hydroxide) which may be seen separating out just before passivity sets in. This separation has been noticed by Hedges,[6] and independently by W. J. Müller who (for reasons to be given later), is not a supporter of the oxide-film view of passivity. Müller[7] has performed at Vienna a number of fruitful researches on the time needed to bring about passivity; when a current is applied the anode does not at once become passive; passivity only sets in after an interval—this interval being short if the current density is very high, and long if it is lower. The interval represents the time needed to produce saturation of the surface layers of liquid.

Isolation of the Film

In my opinion, all the facts quoted can be explained satisfactorily only on the view that passivity is due to a protective film, or something of that nature; the film need not always be an oxide, but apparently it generally is. But it has long been my opinion that little progress is possible without a means of isolating these films from their basis, and studying them in detail. It has already been explained that, while a thin transparent film may be invisible when in optical contact with a brightly reflecting surface, it should become visible if stripped therefrom. Several years ago, I began to look about for methods of removing thin films from metallic surfaces. Success was first obtained in the case of lead,[8] where the low melting point of the metal made it possible to lift off on to glass the films responsible for the brilliant interference colors produced when lead is heated in air. Later,[9] the analogous stripping of oxide films from iron was performed by chemical means; films (of thick-

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[6] E. S. Hedges: *Idem*, 2880.

[7] W. J. Müller: Über die Passivität der Metalle, Speziell des Eisens. *Ztsch. Elektrochem.* (1924) **30,** 401.

Stromdichte, Spannungskurven und Zeiterscheinungen bei Passivierung verschiedener Metalle. *Ibid.* (1927) **33,** 401.

Neue Untersuchungen zur Passivität der Metalle. *Ibid.* (1928) **34,** 571.

Über die Stromdichtepotentialkurven passivierbarer Metalle, am Beispiel des Eisens dargestellt. *Monatshef. f. Chem.* (1927) **48,** 65.

[8] U. R. Evans: The Colours Due to Thin Films on Metals. *Proc.* Roy. Soc. (1925) **107A,** 228.

[9] U. R. Evans: The Passivity of Metals. Part I. The Isolation of the Protective Film. *Jnl.* Chem. Soc. (Pt. I, 1927) 1020.

nesses both above and below the "interference-color range") were isolated from the iron basis by dissolving away the metal below either by iodine or by anodic treatment, thus undermining the oxide skin. The same procedure can be applied to films on copper and aluminum, but it is not specially suited for these metals. The oxide skin on aluminum, however, has been isolated by a much more satisfactory method originally employed by Withey and Millar,[10] but actually applied to the problem under discussion by Sutton and Willstrop;[11] this method consists in heating the specimen in a current of dry hydrogen chloride gas which carries off the aluminum as volatile aluminum chloride, leaving behind the transparent skin of oxide. The oxide skin has also been removed from aluminum by Maass[12] using another method, cathodic treatment; under favorable conditions, the hydrogen bubbles can be made to push the film away from the metal.

I propose, with your permission, to devote some little time to describing the removal of thin films from iron by the two methods which I worked out in 1926, because it is easier to describe phenomena that one has seen with one's own eyes, rather than phenomena of which one has only read in somebody else's paper. It will perhaps be best to commence by describing the isolation of "visible films"; *i. e.*, films of a thickness suited to produce interference tints.[13] A strip of electrolytic iron ground with emery may be heated at one end, to give a sequence of colors, as in Fig. 1, and then cut into pieces representing the different colors. Let us suppose that the piece tinted to the first blue temper color is placed in a concentrated solution of iodine in potassium iodide. During immersion, the iodine slowly eats away the metal just below the oxide film. After about 24 hr., the iodine solution is drawn off and replaced by clean water, and the specimen is swirled round; the oxide film then comes peeling off in fragments which curl up into tight rolls (Fig. 3); these can be washed by repeated decantation, and although they break somewhat during the washing, the pieces finally obtained are large enough to be examined with convenience under the microscope.

There is no doubt that the fragments of oxide films represent the original surface of the iron in an oxidized condition. Viewed by reflected light, the fragments are lustrous, and might well be taken for metal; the surface is corrugated, retaining the grooves and ridges produced by the

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[10] W. H. Withey and H. E. Millar: Determination of Aluminum Oxide in Aluminum Metal. *Jnl.* Soc. Chem. Ind. (1926), **45,** 170 T.

[11] H. Sutton and J. W. W. Willstrop: Nature of the Film Produced by Anodic Oxidation of Aluminum. *Jnl.* Inst. Met. (1927), **38,** 259.

[12] E. Maass: Die Abhangigkeit der Korrosion sursachen des Aluminiums von seiner physikalischen und chemischen Beschaffenheit. *Korr. und Met.* (1927) **3,** 29.

[13] U. R. Evans: Films Responsible for Oxidation Tints on Metals. *Nature* (1927), **120,** 584. The Passivity of Metals.—Part I. The Isolation of the Protective Film. *Jnl.* Chem. Soc. (1927) 1024.

emery grinding upon the original metal; when, however, the system of illumination is changed so as to allow of transmitted light, it is found that the fragments are transparent; when the film is viewed by transmitted light, the "corrugations" are represented by a series of dark lines.

The oxide film removed in the same way from iron tinted merely to a red-brown temper color is essentially similar, but it is thinner and therefore more transparent; the oxide film responsible for the straw-yellow tint is again thinner and more transparent. The really interesting point is reached when the portion of iron strip heated just insufficiently to give the yellow tint—the portion which shows passivity—is treated with iodine by the same method. It is then found that this portion also yields a film, similar to that obtained from the "tinted" regions, but still thinner, and therefore more transparent by transmitted light and considerably less lustrous by reflected light; this film still shows the original abrasion marks as a series of dark lines distinctly visible by transmitted light; evidently we have here the "invisible" film responsible for the passivity, rendered "visible" by removal from the bright basis. When the iodine treatment is applied to portions of the strip at the cold end—portions which do not cause passivity—no peeling off of films can be observed by the naked eye; but careful microscopic study has shown that, even here, minute shredlets of oxide skin do peel off; these are different in appearance to the continuous skin obtained from the passive portion, but clearly represent the beginnings of oxide films which had started to form at different points but which had not properly joined up to constitute a complete covering over the whole surface.

This last observation is of great importance. Evidently even active iron—supposing that it has been exposed to air—has oxide on its surface. The difference between passive and nonpassive iron is that in the former case the skin is sufficiently strong and continuous to protect the metal below, while in the latter case it is not sufficiently strong and continuous—a view long maintained by Haber.[14] This view serves to remove one other objection formerly raised against the idea that passivity is due to an oxide skin. If it were true that passive iron is covered with a film, and that active iron is *completely* free from a film, there should be a measurable difference between the optical properties of the surfaces. Many years ago, Müller and Koenigsberger,[15] using a very sensitive

[14] F. Haber and F. Goldschmidt: Der Anodische Angriff des Eisens durch Vagabundierende Ströme in Erdreich und die Passivität des Eisens. *Ztsch. Elektrochem.* (1906) **12,** 64.

[15] W. J. Müller and J. Koenigsberger: Über das Reflexionsvermögen von passivem Eisen. *Phys. Ztsch.* (1904) **5,** 413.

Optische und elektrische Messungen an der Grenzschicht Metall-Elektrolyt. *Ibid.* (1906) **7,** 796.

Über das Anodische und Kathodische Verhalten von Eisenspiegeln und die Passivität des Eisens. *Ztsch. Elektrochem.* (1907) **13,** 659.

photometer, compared the reflecting powers of iron in the active and passive states, and found that there was—in most cases—no measurable difference. At the time this was regarded by many as fatal to the oxide-film theory of passivity; but if (as is now believed) both active and passive forms of iron have oxide present and only differ in regard to the state of repair, no appreciable difference in the reflectivity need be expected. Actually, the optical question has lately been completely cleared up by some particularly beautiful work in Professor Freundlich's laboratory at Berlin.[16] Mirrors of pure metallic iron were prepared by heating the vapor of iron carbonyl in sealed tubes; no air was admitted to the tubes, so that the mirrors produced were free from oxide. By means of special apparatus, the reflecting properties of these mirrors were very accurately measured. Then air or oxygen was admitted, and almost immediately there occurred a change in the reflecting properties (notably in the phase relations between the two components of the light vibrating in and perpendicular to the plane of incidence); the results indicate the formation of an oxide film, probably about 10 Å thick, and since the chemical properties of the iron undergo a change at the same instant, it is natural to attribute this change to the formation of the oxide film also.

It has been mentioned that the passivity produced by potassium chromate is rather more persistent than that produced by exposure to air. A film can readily be isolated from iron rendered passive by long immersion in potassium chromate, using the iodine method. Some photomicrographs of film fragments thus obtained are shown in Figs. 4 to 8; unlike Fig. 3, these photographs were all taken by transmitted light. The iron was first ground with emery or carborundum, then placed in potassium chromate solution, then washed, and the film separated by means of iodine, washed, dried, and photographed. The dark areas are due to residual metal, or in some cases to grains of abrasive. The series of dark lines represent the original corrugation of the metallic surface left by the abrasive treatment which was applied to clean the surface before the iron was immersed in the potassium chromate solution; it will be observed that the flakes have tended in every case to break in these same directions, so that the edges are themselves parallel to the series of dark lines. Fig. 4 shows the film removed from a piece of iron ground by hand with fine emery flour in two directions roughly at right angles; two sets of fine lines roughly at right angles will be noted. Fig. 5 shows at a lower magnification the film obtained from iron ground with a somewhat coarser emery, in two directions at right angles; the two sets

[16] H. Freundlich, G. Patscheke and H. Zocher: Über die Passivität von Eisenspiegeln. *Ztsch. Phys. Chem.* (1927) **128,** 321; (1927) **130,** 289.

Discussion: Über das Verhalten von Nickelanoden. *Ztsch. Elektrochem.* (1927) **33,** 423.

3 4

5 6

7 8

FIGS. 3–8.—CAPTIONS ON OPPOSITE PAGE.

of coarser lines will be noticed, and also the square shape of some of the fragments, due to breaking parallel to these directions. Fig. 6 shows the film from iron ground with the same emery, but in two directions roughtly at 45°; here the two series of dark lines cross roughly at 45°, and the fragments often show a wedge-shaped outline. Fig. 7 shows a specimen with the final grinding in one direction only. Finally, Fig. 8 shows, at a lower magnification still, fragments of skin obtained from iron ground, in one direction only, with an exceptionally coarse abrasive. Note the parallel sets of elongated rents which have appeared in the skin; these arrived during drying; while wet, the fragments were without holes. This appearance of fissures during drying may possess some significance, because not infrequently iron which is passive when wet is found to become active when it dries.

The author's anodic method of isolating the oxide skin[17] may also be mentioned because it illustrates the surprising strength of this skin. A strip of pure iron may be abraded, rendered passive in potassium chromate, and trimmed along the bottom so as to give an edge free from continuous oxide. It is now made the anode in a solution of potassium chloride, and when current provided by an external battery is passed through the solution, the iron is eaten away from inside the oxide envelope, commencing at the trimmed edge, and gradually advancing upwards. Finally, if disturbance is avoided, we are left with a transparent oxide envelope, consisting of two transparent skins joined together at the edges but open at the bottom; one skin represents the front face of the original iron specimen; the other similarly represents the back surface. There is usually a certain amount of residual metallic iron and secondary products but these do not interfere with the study of the skin. Sometimes the envelope gapes open a little, revealing clearly that it consists of two films, not of one; sometimes rents appear locally in one skin or the other; but on the whole it retains the shape of the original electrode wonderfully well. The skin reproduces the original configuration of the iron surface, and the microscope reveals, as usual, series of lines representing the original abrasive treatment. The fact that the skin—whether isolated by the iodine method or by the anodic method—preserves the shape and markings of the original metal shows that it *is* the original surface of the

[17] U. R. Evans: The Passivity of Metals—Part I. The Isolation of the Protective Film. *Jnl.* Chem. Soc. (Pt. I, 1927) 1022.

FIG. 3.—OXIDE-FILM IN CURLING FLAKES. × 25.

FIG. 4.—FILM FROM IRON GROUND BY HAND WITH FINE EMERY IN TWO DIRECTIONS AT RIGHT ANGLES. × 160.

FIG. 5.—FILM FROM IRON GROUND IN SAME WAY WITH COARSER EMERY. × 40.

FIG. 6.—FILM FROM IRON GROUND WITH COARSE EMERY IN TWO DIRECTIONS AT 45°. × 40.

FIG. 7.—FILM FROM SPECIMEN GROUND IN ONE DIRECTION. × 40.

FIG. 8.—FRAGMENTS OF FILM FROM IRON GROUND WITH EXCEPTIONALLY COARSE ABRASIVE, IN ONE DIRECTION ONLY. × 25.

metal converted into oxide, and not something laid *upon* the original surface.

The Corrosion of Metals

The experiments described indicate clearly that the oxide film to which the passivity of iron has long been ascribed has a real, and indeed a wonderfully robust, existence. It is now possible to consider the part played by this skin in some of the phenomena of corrosion. The subject of corrosion is far too large a subject to cover in a single lecture. I have discussed it both in its academic and its engineering aspects in a series of papers published elsewhere.[18] It is merely possible today to take a few typical examples illustrating the principles involved. In providing the experimental basis for these principles, researches carried out in the United States have played a very notable part. The paper published by J. Aston,[19] in 1916 is one of the most important landmarks on the winding road that leads to the understanding of corrosion. The work of McKay,[20] Whitman and Russell,[21] Speller,[22] Pilling and Bedworth,[23] and many others will long be remembered, and I only regret that it is impossible at this time to discuss the results reached by these various investigators.

It is well established that the corrosion of iron by most natural waters proceeds quickly only if a supply of oxygen is provided, but that, as a rule, the actual seat of corrosion is not the place where oxygen is present in greatest concentration. For instance, if we partly immerse a sheet of clear steel in a vertical position in an (unstirred) solution of salt (sodium chloride), for a few days, it will be found that the zone immediately below the water line (the part most accessible to oxygen) has remained bright and uncorroded, but that a little lower down the metal has been distinctly attacked. This indicates that the *direct* effect of dissolved oxygen is not to produce corrosion but rather to prevent or at least to divert it. The steel, before ever it enters the liquid, has the rudiments of an invisible oxide skin on it, but the skin present on steel is not sufficiently sound to prevent corrosion altogether. When the steel is

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[18] For summary, see: U. R. Evans: Corrosion of Metals, 2d Ed., New York, 1926. Longmans Green & Co.

[19] J. Aston: Effect of Rust upon the Corrosion of Iron and Steel. *Trans.* Amer. Electrochem. Soc. (1916), **29**, 449.

[20] R. J. McKay: Corrosion by Electrolyte Concentration Cells. *Trans.* Amer. Electrochem. Soc. (1922) **41**, 201.

[21] W. G. Whitman and R. P. Russell: The Acid Corrosion of Metals. Effect of Oxygen and Velocity. *Ind. & Eng. Chem.* (1925) **17**, 348.

[22] F. N. Speller: A Study of Corrosion Factors and the Electrochemical Theory. *Ind. & Eng. Chem.* (1925) **17**, 339. Also Corrosion—Causes and Prevention. New York, 1926. McGraw-Hill Book Co.

[23] N. B. Pilling and R. E. Bedworth: The Oxidation of Metals at High Temperatures. *Jnl.* Inst. Met. (1923) **29**, 529.

placed in position in the liquid, the dissolved oxygen present in excess near the water line keeps the skin over this region in fairly good repair, and the attack is therefore *diverted* to the part lower down, where the supply of oxygen is insufficient for repairing purposes.

This diversion occurs in a very interesting way. The electric potential of the portion near the water line covered with a film in good repair is appreciably different from that of the portion lower down; measurements by McAulay and Bowden[24] in the University of Tasmania have

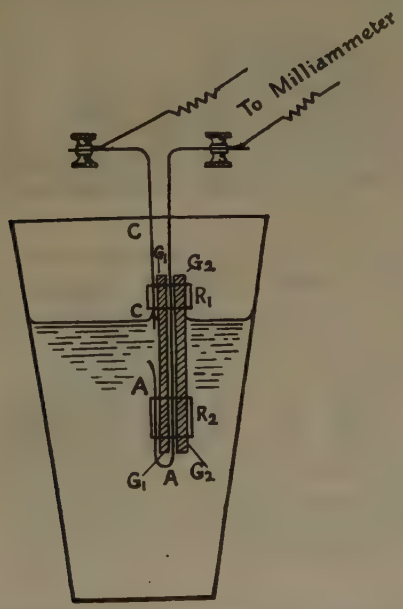

FIG. 9.—DEMONSTRATION OF FLOW OF ELECTRIC CURRENT BETWEEN UPPER AND LOWER PARTS OF SPECIMEN.

(Reprinted from U. R. Evans' book, The Corrosion of Metals, by permission of the publishers.)

indicated that the difference between the potentials over these two regions is often about 0.2 volts; recent researches in Cambridge have shown that under special circumstances as much as 0.45 volts may be set up by differences in oxygen supply. As a consequence of these differences of potential an electric current flows between the "aerated" zone near the water line, which forms the cathode and is unattacked, and the "unaerated" zone below, which is the anode and suffers corrosion. A continuous supply of oxygen to the upper (cathodic) part is needed if the current is to continue to flow, but the corrosion con-

[24] A. L. McAulay and F. P. Bowden: An Investigation of the Effect of Differential Aëration on Corrosion by Means of Electrode Potential Measurements. *Jnl.* Chem. Soc. (1925) **127**.

nected with the current occurs at the places to which oxygen is *not* supplied. The currents set up by differences in oxygen supply are known as "differential aeration currents," and are of exceptional importance in corrosion processes.

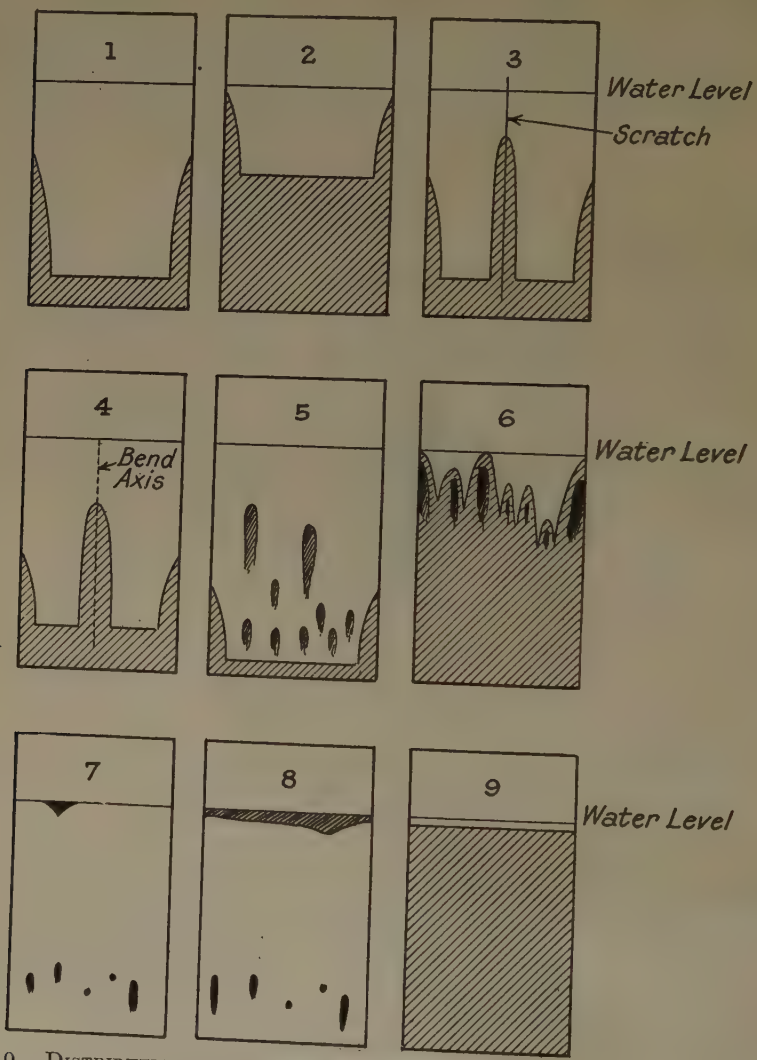

FIG. 10.—DISTRIBUTION OF CORROSION PRODUCED ON PARTLY IMMERSED SPECIMENS OF IRON AND STEEL.
Corroded parts, shaded or dark; uncorroded, white.

The effect of the electrolysis of sodium chloride between steel electrodes is, of course, to produce sodium hydroxide at the cathodic area (above), and ferrous chloride, by the corrosion of the metal, at the

anodic area (below); where they meet, these two substances interact to produce ferrous hydroxide, which is quickly oxidized to the dark greenish ferroso-ferric hydroxide, and usually then (at least in part) to the brown ferric hydroxide. The mixture of iron hydroxides produced is commonly known as "rust." It should be noted that *rust is not the direct oxidation product of the metal, but is a precipitate formed by secondary reactions;* the direct product is the invisible film (comparable, in some ways, to the thicker oxide scale produced when iron is heated strongly in air, but quite unlike rust). The actual reactions by which rust is produced vary with the nature of the water, but it is important to remember that it is *never* the *direct* oxidation product of the metal.

The flow of electric current between the upper and lower parts of the specimen can be directly demonstrated (Fig. 9), if, before the experiment, we cut our specimen into two halves, clamping the upper half *C* vertically so that the bottom edge just passes below the water surface, and arranging the other half *A* a little below it; if the two halves be now joined to a milliammeter, the current, generated simply by differences of oxygen concentration, can be measured on the instrument.

I would emphasize the fact that *each step in the corrosion process just described has been directly demonstrated by experiment;* the formation of alkali near the water line and of ferrous chloride at the lower parts can be ascertained simply by taking samples of the liquid from these points and applying simple chemical tests; the formation of rust at the places where these two primary products meet and interact is directly visible to the eye. The electric current can be tapped and measured by the method already indicated. It is therefore quite wrong to refer to the mechanism described above as a *theory* of corrosion. The description represents not theories but facts, established on far more direct evidence than the majority of statements accepted without question by each one of us in our everyday life.

The Distribution of Attack

It is now possible to look a little more closely into the factors determining the distribution of the corroded and uncorroded areas. Fig. 10 shows the distribution of corrosion produced on partly immersed specimens of iron or steel under different conditions. If a specimen of steel is cut and carefully cleaned by abrasion and kept in dry air for, say, 24 hr., with care to avoid undue bending, and if it is then partly immersed in sodium chloride solution, corrosion may at first be confined to the edges and bottom, as in specimen 1; the edges represent places where the stresses left by cutting keep cracking the protective film, while the bottom represents the place least accessible to repairing oxygen. The corroding area from the bottom advances steadily upwards with the

time, the boundary between the corroded and noncorroded area being usually horizontal and practically straight; in due course we reach the stage represented by specimen 2.

But if, just before the immersion, the specimen is violently scratched locally with a jagged edge, say of carborundum, or if it is bent along a central axis, corrosion will also set in along the scratch line (specimen 3) or along the bending line (specimen 4). Frequently the corrosion along these lines may extend to the water level in the early stages, but owing to the good supply here of repairing oxygen, attack does not usually continue at the water line itself, and in the later stages, the corroded area does not come quite as high as the water level; of course, the exact state of affairs depends on the character of the bending or scratching.

The distribution of corrosion shown in specimens 1 and 2 represents an ideal case, often realized if the specimen is free from surface flaws, and if it is handled with care to avoid bending. In general, however, in addition to corrosion starting from points on the edges and along the bottom, corrosion will be found to start at points in the center representing weak places in the oxide film (specimen 5). These central points of corrosion may sometimes represent pores in the metal, whose interiors will be less accessible to oxygen than the main part of the surface, or they may represent surface defects left by the original rolling; or again they may represent places where the abrasion, used for cleaning the metal, has left exceptionally deep depressions, or exceptionally serious stresses; or perhaps they may sometimes represent the site of inclusions, the edges of which will serve as vulnerable spots in the protective skin. Whatever cause may be operative, corrosion sets in at these "weak spots," and the loose rust (formed by interaction between the ferrous chloride produced by the corrosion and the sodium hydroxide produced at the cathodic area around and above) streams down and covers the metallic surface below; the portion thus covered by loose rust is screened from the action of repairing oxygen, and becoming anodic towards the rest of the metal, begins in its turn to suffer corrosion. At first it is only the weak points in the *lower* part of the specimen which suffer attack (specimen 5), but later on, as the oxygen is used up in the corrosion process, the repairing forces at the higher levels become enfeebled, and rust begins to stream down from isolated points in the high portions also. Finally, practically the whole immersed area comes to be blanketed with loose rust, and over the whole of the blanketed area, the steel suffers corrosion, becoming visibly etched (specimen 6); the corrosion is most intense just below the "arches" of the corroded area, the portions shown darkest in the diagram; on the other hand, the small cathodic area at the water line retains its original surface, quite unetched and without perceptible corrosion. In these later stages, the alkali formed at the cathode creeps up above the water line, producing an upward extension of the cathodic area; this

enables the anodic area to advance high enough to touch the water line itself at many points.

In stagnant water, therefore, the corrosion usually starts locally at isolated points, and spreads out until it affects nearly the whole immersed area; it should be understood that this extension of corrosion is due to the fact that the rust from the points originally attacked spreads down, and, excluding the oxygen which alone can keep the invisible protective oxide film in repair, permits the enlargement of the area undergoing attack. If the liquid is kept in rapid motion, the rust may be swept away, and will only adhere just at the spot undergoing attack. Then corrosion remains localized, producing a limited number of deep pits each covered with a blister of membranous rust, the hydroxide membrane being formed by interaction between the soluble iron salt formed within the pit and the alkali formed outside. The intensity of the local attack is due to the fact that the stirring ensures a rapid renewal of dissolved oxygen to the large cathodic area, and since the whole effect of the corrosion is concentrated on the small part within the blister, the rate at which the attack bores into the metal is pronounced. These rust blisters, each covering a deep pit, are often seen in pipes and water jackets, usually arranged in rows, and frequently elongated in the direction of water flow.

In stagnant salt water, iron or steel suffers no special corrosion at the water line. Owing to the fact that there is a better supply of oxygen here than anywhere else, this portion is immune from attack; so immune is the water line from attack that often, after a piece of steel partly immersed for some days in stagnant salt water has been taken out and dried, it is impossible to decide definitely up to what level the water had come. It may be thought at first that this is contrary to the common experience of marine engineers who in practice find much trouble at the so-called "wind-and-water line." It must, however, be remembered that on metal work partly immersed in the sea the water level is constantly changing, and most of the corrosion found at the wind-and-water line has actually been produced at moments when the places in question were wetted with water-drops, but exposed to air, the true water line being (temporarily) lower down. The whole question is often complicated by the fact that iron work exposed to the sea is usually painted, and that the paint itself will be attacked most readily at the place where water, air, light and alkali simultaneously act upon it. This question is too complicated to be considered. It will suffice to say that the "wind-and-water" corrosion of the marine engineer is not strictly "water-line" corrosion in the sense used by the chemist.

Nevertheless true water-line corrosion is sometimes met with on steel. It was stated in the early part of the lecture that a protective film is more likely to break down at a boundary between different phases than

elsewhere; it is specially liable to break down at the water line, where capillary forces may cause the protective film to leave the metallic surface and cling to the air-water interface, thus leaving the metallic surface unprotected. In a rapidly corroding solution, this is unlikely to occur, since the rapid corrosion uses up oxygen very quickly; and since the water line is the only place where constant renewal of oxygen is possible, this portion is kept in better repair than the part lower down. Consequently the breakdown of the skin invariably occurs over the lower part, and this very fact renders "leakage" through the skin along the water line improbable. But if we reduce the rate of total corrosion, and consequently the rate of oxygen consumption, there will be no great discrepancy between the oxygen concentration in the higher and lower levels. Under such circumstances, the special liability for the skin, as it were, to "come unstuck" along the water line becomes important, and true water-line attack often develops. Thus aluminum, which suffers much less rapid corrosion than iron, shows special attack at the water level in a chloride solution. Again, the various corrosion-resisting steels containing chromium, or chromium and nickel, if they are attacked at all, often suffer along the water line. Ordinary steel suffers no water-line corrosion in a plain sodium chloride solution, but it may be attacked along the water line if certain substances, such as sodium carbonate or phosphate, are added which reduce the amount of total corrosion; if either salt is added in an amount sufficient greatly to reduce corrosion, but not quite sufficient to prevent it, the small amount of corrosion which does occur is largely concentrated at the water line (see specimen 7, representing an early stage, and specimen 8 representing a later stage).

The reason why these salts reduce corrosion is quite simple. The carbonate and phosphate of iron are almost insoluble, and the effect of the anodic attack of iron in presence of these salts is to convert the surface of the iron to an insoluble substance; in other words, any anodic reaction which commences at the weak spots will tend automatically to repair these weak spots and thus to bring the corrosion to an end. But it should be noticed that the addition of these substances is not only to reduce the total amount of corrosion but also to restrict the area undergoing corrosion. Usually the reduction of area is more marked than the reduction of total corrosion and therefore the *intensity* of the attack (*i. e.*, the corrosion per unit area of the parts affected) will actually be greater than if no phosphate or carbonate had been added. Of course, if a large amount of phosphate or carbonate is added, attack may be prevented altogether; but an insufficient quantity may cause perforation of an iron specimen to take place more quickly than if no addition had been made. This has a bearing on the practical employment of such substances as additions to chloride waters which are to flow through cooling jackets.

Phosphates and carbonates reduce corrosion because the direct *anodic* product is a nearly insoluble body. On the other hand, solutions of calcium and magnesium salts reduce corrosion because the direct *cathodic* product (calcium or magnesium hydroxide) is nearly insoluble, and screens the metal from oxygen; as a result hard waters containing calcium and magnesium salts produce less corrosion at ordinary temperatures than soft waters, although the chalky scale of calcium or magnesium compounds may be objectionable in other ways. At high temperatures, salts of calcium and magnesium suffer hydrolysis, yielding free acid which can attack metal readily even in the absence of oxygen, and thus accelerate the attack; in boilers, for instance, magnesium chloride is an exceptionally objectionable constituent of the feed water.

The distribution of corrosion on steel immersed in a magnesium sulfate solution is interesting (specimen 9). Since the cathodic product (magnesium hydroxide) is capable of screening the metal from oxygen, it is clear that any place where it is deposited soon ceases to be cathodic and becomes anodic; in a short time, therefore, practically the whole immersed area has become anodic, and the only cathodic (uncorroded) area is a thin straight strip within the meniscus at the water line; this strip receives a sufficient supply of oxygen, notwithstanding the white magnesium hydroxide which accumulates here.

The idea may suggest itself, that, since the direct action of oxygen is not to produce corrosion, but to confer local immunity, it should be possible to prevent corrosion altogether by ensuring a supply of oxygen everywhere. This is not quite such a simple matter to bring about as may appear at first sight, but it is possible to show[25] that when a disk of pure, electrolytic iron is whirled in a special apparatus in laboratory distilled water containing oxygen, it remains practically unchanged, although the same iron placed half immersed in the same water rusts quite readily; here conditions of *uniform aeration* give *immunity*, while conditions of *differential aeration* cause *corrosion*. But with steel it is more difficult to obtain immunity in this way; as already stated, the film on steel is always less reliable than that on pure iron. It is true that when water is made to flow with great velocity over steel, the total corrosion is less than if it flows fairly slowly; this fact—noted by Heyn and Bauer[26] and by Friend[27]—is no doubt due to the fact that a good uniform supply of oxygen is brought to almost all points of the surface.

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[25] U. R. Evans: Corrosion of Metals, 2d Ed., 108. New York and London, 1926. Longmans Green & Co.; Edward Arnold & Co.

[26] E. Heyn and O. Bauer: Über den Angriff des Eisens durch Wasser und Wässerige Lösungen. *Mitteil.* a. d. Kgl. Materialprüfungsamt zu Gross-Lichterfelde West. [Berlin] (1910) **28**, 93, 130.

[27] J. A. N. Friend: A Colloid Theory of the Corrosion and Passivity of Iron and of the Oxidation of Ferrous Salts. *Jnl.* Chem. Soc. (1921) **119**, 932.

But with steel it seems impossible to prevent corrosion altogether, and the corrosion which does occur is concentrated on a few points, where rather rapid pitting occurs. If, however, in place of oxygen we use potassium chromate, which is more soluble and gives a more reliable film, as already stated, corrosion may sometimes be prevented altogether. The addition of chromates to water used in cooling jackets and also to refrigerating brine is practiced with success in several places in the United States and will be familiar to many.

Other Types of Attack

There are many other types of corrosion which can be mentioned here, but cannot be discussed. Even in the absence of oxygen, some attack can still occur, iron passing into solution and replacing hydrogen. This occurs comparatively rapidly in acid solutions, but it may be appreciable in neutral or even in alkaline solution. The recent and extensive work of Baylis[28] on the water supplies of several cities in the United States has indicated the importance of the hydrogen-evolution type of corrosion in the internal wastage of pipes, while the investigations of Shipley, McHaffie and Clare,[29] in Canada have shown that in certain soils the same mechanism may bring about external corrosion also. Finally, the recent researches of Thiel[30] and others in Germany have disclosed the great importance of the hydrogen-evolution type of corrosion in boilers.

Passing from conditions where oxygen is absent to the other extreme where oxygen is in great excess, one comes to the atmospheric rusting of iron. This occurs only if actual condensation of moisture occurs on the metal, or if hygroscopic dust settles upon it; Vernon[31] has shown that the rusting of iron in an indoor atmosphere is practically prevented if the iron specimens are placed in a muslin cage, which filters out the dust. Deposition of pure water on iron does not cause rapid rusting but if the moisture contains salts or acids corrosion is greatly accelerated. Hence the presence of acid fumes, or of sea spray, greatly enhances the rusting properties of damp air. Particularly dangerous are bodies which are hygroscopic, or which form hygroscopic bodies by acting on iron, since then the surface will remain wet even on dry days; in this respect, iron which has once been exposed to sulfuric acid fumes, or iron which has at

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[28] J. R. Baylis: Factors Other Than Dissolved Oxygen Influencing the Corrosion of Iron Pipes. *Ind. & Eng. Chem.* (1926) **18,** 370.

[29] J. W. Shipley, I. R. McHaffie and N. D. Clare: Corrosion of Iron in Absence of Oxygen. *Ind. & Eng. Chem.* (1925) **17,** 381.

[30] A. Thiel and H. Luckmann: Über Korrosions-erscheinungen. *Korr. und Met.* (1928), **4,** 169.

[31] W. H. J. Vernon: Relative Behaviour of Copper, Zinc, and Brass Exposed to Several Types of Indoor Atmospheres. *Trans.* Faraday Soc. (1927) **23,** 160.

any time been immersed in the sea, is especially liable to atmospheric rusting.

One more question may be discussed before the lecture closes: Has rust a protective action, or does it stimulate further rusting? We have seen that the *invisible* oxide film which is the *direct* product of oxidation at ordinary temperatures is definitely protective to the iron immediately covered by it; likewise, a directly formed film of iron phosphate, produced by anodic action of iron in a sodium phosphate solution, is protective; clearly the conversion of the surface layers of the metal *in situ* into oxide, or phosphate, must tend to protect the metal below. But rust is not a direct product; it is a precipitate formed, as we have seen, by secondary reactions, and usually at a sensible, although often microscopic, distance, from the actual seat of corrosion. It is not protective in the sense that the invisible directly formed oxide is protective.

Nevertheless a layer of rust may often have a retarding action on further corrosion. Supposing a piece of iron totally immersed becomes wholly covered with rust, this will screen the metal from dissolved oxygen, and corrosion must therefore be very slow; for corrosion—to be rapid—requires the presence of oxygen at some point on the metal, although not at the actual seat of corrosion. Thus a *complete* rust covering may be said to *retard* further rusting. But now consider a case where the article is only partly covered with rust. Here oxygen can reach the rust-free part, which will function as cathode and will produce anodic attack to the metal where it is shielded from oxygen by the rust; in this case, it would be true to say that a *partial* rust-covering *promotes* further rusting on the rusted part. This explanation of the action of rust on rusting was first made clear by J. Aston.[32] In atmospheric corrosion, rust promotes further rusting for quite a different reason, namely because a rusty surface will remain wet for a considerable period after a rust-free surface has dried up.

It will be evident that relatively small changes in the conditions have an enormous influence on the phenomena of corrosion. The reasons for this apparent irregularity in corrosion results are fairly well understood; indeed, there is now far better agreement among investigators—at least as far as the basic mechanism of corrosion is concerned—than could have been hoped for by the most optimistic observer eight years ago. While much remains to be investigated, there is good reason to expect that future progress will be rapid. Perhaps one of the most helpful features of recent years is the increasing desire of scientists and engineers of different countries to "get together and compare notes." Your Institute has played a conspicuous part in developing a policy of international cooperation among scientists. In a recent and very cordial letter addressed to the Institute of Metals in London, you said that

[32] J. Aston: *Op. cit.*

Science knows no Boundaries. No better motto could be found for your endeavors. I think that these sentiments find strong support in scientific circles in Britain, and also in other European countries with which I am acquainted. Indeed the truth of your words has been particularly apparent at numerous scientific gatherings held recently in Europe, at which scientists belonging to a dozen or more of different nations have contributed to the discussion—to the great advantage of all. Scientific acquaintances often develop into warm personal friendships, and it is evident that the benefits derived from this sort of intercourse will not be confined to Science, but that they may represent a very definite contribution to the Peace and Happiness of the World.

Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions

By G. D. Bengough,* J. M. Stuart* and A. R. Lee,* Teddington, Middlesex, England

(New York Meeting, February, 1929)

Corrosion tests should be designed so as to facilitate as far as possible the interpretation of results, consequently factors which may affect the rate of corrosion should be controlled as far as practicable, and very full data should be given regarding the conditions of the test. Among the most important factors affecting the rate of corrosion is often the rate of supply of oxygen to the metal surface. It is essential therefore to understand the mechanism by which oxygen is transferred from the liquid surface to the surface of the metal. The work of Adeney and his coworkers has thrown much light on this mechanism. They have shown[1] that the aeration of deaerated water and salt solutions proceeds much more rapidly than can be accounted for by mere diffusion, and have suggested that downward "streaming" takes place from the surface of the water, due mainly to an increase of density brought about by evaporation. The evaporation reduces the temperature of the surface layer, and also increases the concentration in the case of salt solutions. The effect of evaporation in facilitating the transfer of oxygen to a metal and increasing the corrosion of the metal was shown in some experiments due to Friend.[2] He tested the corrosion of mild steel plates immersed in water in glass jars, a steady stream of air being drawn over the surface of the water in the jars. The air passing through half the number of jars was saturated with moisture, that passing through the others was dried with calcium chloride. He found that "in every case the water exposed to dry air was approximately twice as corrosive as that exposed to air saturated with water vapor."

Conditions for Quantitative Corrosion Tests

These results show that we must either control or prevent evaporation at the liquid surface, if we wish to avoid effects on the rate of cor-

* The Chemical Research Laboratory.

[1] W. E. Adeney, A. G. G. Leonard and A. Richardson: Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride. *Phil. Mag.* (1923) **45**, 835.

[2] J. A. N. Friend: Corrosion of Iron in Water and in Neutral Salt Solutions. *Jnl.* Chem. Soc. (1923) **123**, 2996.

rosion due to causes independent of the corrosion process itself. It is simpler to prevent evaporation than to control it, since evaporation can be prevented if the gas and solution are kept at the same temperature and the gas is saturated with water vapor at the vapor pressure of the solution.

If the solution is stirred or aerated instead of kept stagnant, the effect of the increased oxygen supply on the rate of corrosion may be even more striking. Rawdon and Groesbeck[3] find the following percentage increases in the rate of corrosion of various metals due to aeration in simple immersion tests in sodium chloride solutions:

Metal	Percentage Increase
Nickel	8
Monel metal	−40
Copper-nickel alloy	26
Admiralty nickel	81
Copper	662

Besides controlling the conditions affecting the rate of oxygen supply, the test conditions should insure that as far as possible the solution contains only substances deliberately introduced for the test and those resulting from the corrosive action. The ordinary corrosion test conducted in open vessels fails conspicuously in this respect. An aqueous solution exposed to the ordinary atmosphere will tend to absorb carbon dioxide, and if this produces corrosion and is removed from solution, more carbon dioxide from the air will take its place. Other gases and even dust may find their way into the solution, introducing traces of various impurities.

In the ordinary corrosion test, the shape, dimensions and composition of the metal specimen are usually stated. The depth of immersion is sometimes given, but owing to lack of appreciation of the importance of specifying factors affecting the rate of diffusion of oxygen, the size and shape of the vessel containing the metal and the solution are often omitted from the description of the test. The latter particulars, however, may prove to be of considerable importance if an attempt is made to repeat the test. The following conditions should be defined for all quantitative corrosion tests:

1. The size, shape, composition and surface treatment of the metal specimen.
2. The depth of immersion and mode of suspension of the specimen, the volume of the solution and the dimensions of the containing vessel.
3. The initial composition and concentration of the solution and gas.
4. The constant temperature and pressure at which an experiment is performed.

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[3] H. S. Rawdon and E. C. Groesbeck: Effect of Testing Method on Determination of Corrosion Resistance. U. S. Bur. Stds. *Tech. Paper* 367 (1928).

The gas should be saturated with water vapor with respect to the solution. Any stirring or aeration used should be completely specified. Nos. 3 and 4 of the list necessitate that the experiment be carried out in a closed space instead of open to the atmosphere.

Measurement of Amount of Corrosion

Three general methods have been used in estimating corrosion and these depend on:

1. Measurement of change of weight.
2. Determination of the amount of metal in the corrosion product after solution.
3. Gas measurement (mainly of oxygen absorption).

Regarding item 1, if the corrosion takes place in such a manner that the corrosion product adheres tightly to the metal and is of uniform composition, the corrosion may be estimated by the increase in weight of the specimen. If this method is used for wet tests the specimen must be dried before weighing. The method is of limited application but is used in atmospheric corrosion tests for accurate work and for certain aluminum alloys in salt solutions for technical purposes.[4]

The method most generally used is the loss-of-weight method. The specimen is weighed before the corrosion test. After the test the corrosion products are removed by rubbing or solution, the specimen is dried and then weighed again. If heavy pitting has occurred, corrosion products tend to remain in the pits even after rubbing, so that the solvent method must be employed. A correction may then be necessary for the metal attacked by the solvent during the removal of the corrosion products. The present authors have used two methods of determining the correction for zinc. In the first method, the corrosion product was removed by immersion in acid for a measured time, the specimen was weighed and again placed in acid for a similar time, dried and weighed. The second loss of weight subtracted from the first gave the "corrected loss of weight." In the second method the hydrogen gas evolved during the removal of the corrosion products was collected and measured. From this the amount of metal attacked by the acid was calculated and deducted from the apparent loss of weight. Care was taken in applying this method to insure that any gas given off by the corrosion products themselves (*e. g.*, CO_2) was not measured as hydrogen.

Method 1 has been used by the authors only for the purposes of comparison with the more informative method 3. Several modifications of method 1 have been carefully studied by Committees B-3 and A-5 of the American Society for Testing Materials.[5] The great difficulty is

[4] D. Basch and M. F. Sayre: Resistance of Various Aluminum Alloys to Salt-water Corrosion. *Mech. Eng.* (1924) **46**, 199.

[5] Report of Committee B-3, Amer. Soc. Test. Mat. (1927).

the lack of agreement between duplicates, and the need of using very large numbers of specimens to define curves for corrosion rates.

Method 2 has been used by Shipley and McHaffie and by U. R. Evans; it has not been used by the authors, since it suffers from drawbacks similar to those of method 1 from their particular point of view.

Method 3 has been employed by Arndt and others in rough laboratory corrosion tests on iron, and Speller and Kendall[6] have used it in investigating the corrosion of steel pipes. Their method consisted in determining the fall in concentration of oxygen dissolved in the water passing through the pipe. Speller has pointed out the advantages of the method for the construction of "time-corrosion rate curves."[7] Whitman and Russell[8] have used the same principle for estimating the corrosion of metal plates in a "corrosion cell," through which water or solutions can be made to flow.

The authors have used the gas-measurement method for accurate laboratory tests on the corrosion of zinc in conductivity water and salt solutions. Zinc disks were supported in stagnant salt solutions initially saturated with oxygen at a pressure of 760 mm. Oxygen gas at a similar pressure was in contact with the solution, and the gas absorption was measured at intervals.

The great advantage of the oxygen-absorption method over the loss-of-weight method is that the course of a corrosion experiment can be followed without disturbing the metal specimen which yields a rate curve for a particular solution in the conditions of the experiment. The loss-of-weight method requires a separate specimen for each point on the curve.

The oxygen-absorption method suffers a complication when applied to a metal having more than one valency; *e. g.*, iron. The distribution of the iron between ferrous and ferric states must be determined in order to estimate the corrosion. Shipley and McHaffie[9] measured oxygen absorption and also determined the iron corroded by method 2. Speller and Kendall[10] determined the amount of ferrous iron in the rust by analysis. In their experiments in flowing water at 80° F., about 30 per cent. of the iron in the corrosion products was in the ferrous state at the end of the experiment, but it dos not follow that this was the case throughout

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[6] F. N. Speller and V. V. Kendall: A New Method of Measuring Corrosion in Water. *Ind. & Eng. Chem.* (1923) **15**, 134.

[7] F. N. Speller: Corrosion Causes and Prevention, 223. New York, 1926. McGraw-Hill Book Co.

[8] W. G. Whitman and R. P. Russell: Natural Water Corrosion of Steel in Contact with Copper. *Ind. & Eng. Chem.* (1924) **16**, 276.

[9] J. W. Shipley and I. R. McHaffie: Relation of Hydrogen Ion Concentration to the Corrosion of Iron. *Canadian Chem. & Met.* (1924) **8**, 121.

[10] F. N. Speller and V. V. Kendall: *Op. cit.*

the experiment. Under stagnant conditions the proportion of ferrous iron might be very different, and would have to be determined at intervals.

Hydrogen gas may be evolved during corrosion in salt solutions by strongly anodic metals such as zinc and iron, and this must be estimated both because of the corresponding corrosion and because a correction for it must be applied to the apparent oxygen absorption.

Application of Gas-measurement Method to Corrosion of Zinc

The gas-measurement method used by the present authors in their study of the corrosion of zinc permits a high degree of control of the conditions previously laid down for quantitative tests.

The principle of the apparatus is shown in Fig. 1. This is a diagram only.[11] A dimensioned drawing of the apparatus appears in the earlier

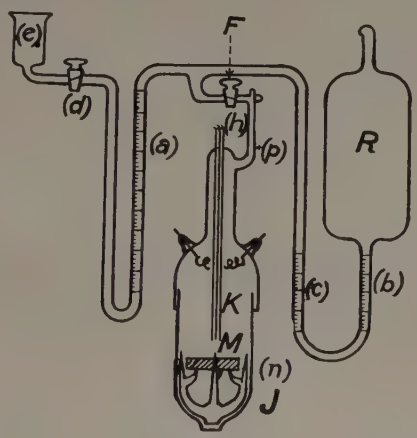

Fig. 1.—Oxygen-absorption apparatus.

paper referred to. J is the corrosion vessel, in which is a glass stand carrying the metal disk M. The glass stand is so constructed as to bring the top of the specimen to a definite distance below the end of the capillary h when the vessel J is pushed into the ground joint connecting it with the rest of the apparatus. This ground joint is sealed with wax for an experiment. The solution is introduced through the capillary h, and any excess of solution is driven back through h (by oxygen pressure). Thus the position of the lower end of h determines the position of the surface of the liquid. It is simple to arrange the construction so that a definite volume of solution (usually 100 c.c.) is left in the vessel J and that the top surface of the metal is immersed to a definite depth (usually 1.5 cm.).

[11] For a full description of the authors' methods of work and numerous results, see: Theory of Metallic Corrosion in the Light of Quantitative Measurements. *Proc.* Roy. Soc. (1927) **116A,** 425; *Idem* (1928) **121,** 88.

In the tests to be described, the atmosphere above the solution consisted of purified oxygen gas. *R* is a manometer bulb also filled with oxygen, and adjusted to a pressure of 760 mm. when at the temperature of the experiment and with the water levels equal in *c* and *b*. If oxygen has been absorbed from the gas in the corrosion vessel, the liquid level will rise in *c* when the tap *F* is opened. Oxygen can then be displaced from the graduated tube *a* by water from *e* till the manometer levels are again equal, thus restoring the gas in the corrosion vessel to its original pressure. The volume of oxygen necessary is equal to that absorbed during corrosion. The apparatus, including the manometer and gas burette, is placed in a thermostat at 25° C., and is therefore at constant temperature and pressure except for the pressure changes due to absorption of gas in the corrosion vessel. Since the gas was usually replaced every 24 hr. during active corrosion, the pressure changes were relatively small.

It was found during the course of the work that hydrogen gas was evolved during the corrosion of zinc in potassium chloride solutions of concentration N/10,000 or greater, in the conditions of the test. It was essential to estimate this hydrogen during the course of a corrosion test in order to obtain the true oxygen-absorption curve, since the observed oxygen absorption is too low by the volume of hydrogen evolved. The hydrogen estimation was carried out by heating the platinum wire shown in Fig. 1. This was done directly after an oxygen measurement, and the hydrogen was calculated from the further contraction obtained (after cooling). This also permitted the construction of hydrogen-evolution and total-corrosion curves, the latter representing the metal corrosion due to both oxygen absorption and hydrogen evolution.

Preparation of Materials for the Test

The zinc generally used was Australian electrolytic zinc of about 99.99 per cent. purity. It was cast into short rods which were sawn up and turned into disks 2.5 cm. dia. and 0.6 cm. thick. For the final turning the specimen was held in a split chuck lined with filter paper and subsequently was handled with filter paper until it was introduced into the apparatus for the corrosion test. Great care was taken throughout the preparation of the specimen to prevent contact with any trace of oil.

In one test "spectroscopically pure" zinc was used, which the New Jersey Zinc Co. had kindly supplied. This arrived from America in the form of rods about 0.8 cm. dia. A portion of rod of about the same total surface as a standard specimen was broken off and used for a corrosion test without further treatment.

Early in the course of the work it was found that annealing of the zinc specimens was necessary in order to insure consistent results from

corrosion tests. The specimens are usually annealed at a temperature of about 250° to 260° C. To hinder volatilization and to avoid the formation of tarnish films on the metal during annealing the specimens were sealed into glass tubes filled with argon before annealing. It was found necessary to exhaust and thoroughly heat the glass tube containing the specimens before filling it with argon. While each end of the glass tube was heated in this way the zinc specimens were kept at the other, cool, end of the tube. Before this procedure was adopted some trouble was experienced through tarnish films forming on the zinc during annealing. Possibly this was due to water vapor, which appeared to come from the glass during the sealing of the large tube containing the specimens, though this tube had previously been carefully dried.

The solutions used were made up with conductivity water prepared in a special still,[12] the conductivity varying from 0.047×10^{-6} to about 0.10×10^{-6} mho (measured on the still cell). The water was collected and the solution made up in a special vessel in contact with purified air. This vessel was subsequently placed in a thermostat, with the corrosion apparatus, and was connected to the latter and to the oxygen supply connections. The latter were arranged so that the solution could be saturated with purified oxygen at a pressure of 760 mm. Then the solution was driven over by the oxygen into the corrosion vessel through the capillary *h* (Fig. 1), the excess being driven back through *h* and the capillary finally sealed off. The solutions used were mainly potassium chloride solutions of concentrations varying from N/100,000 to normal.

Before each test the corrosion vessel *J* and the glass stand were cleaned in concentrated nitric acid and washed with distilled water. The corrosion vessel was steamed for some time. The vessel containing the solution was originally cleaned with concentrated nitric acid and washed, and was again well washed with conductivity water before each solution was prepared.

Results of Experiments

The corrosion of zinc in conductivity water and oxygen is shown in Fig. 2. The mean of the best results for conductivity water gave a corrosion of approximately 1 mg. in 50 days. This is about three times that theoretically possible in pure water[13] as calculated from a determination of the solubility of zinc hydroxide in water at 25° C. (containing oxygen). The additional corrosion indicates the presence of a trace of soluble impurity which probably enters the corrosion vessel as dust, etc., on the surface of the metal specimen or corrosion vessel.

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[12] G. D. Bengough, J. M. Stuart and A. R. Lee: Routine Preparation of Low-conduction of Water. *Jnl.* Chem. Soc. (1927) 2156.

[13] On the assumption that pure water is dissociated sufficiently to conduct electricity.

The corrosion in conductivity water is small, however, compared with that which occurs even in very dilute potassium chloride solutions. This is shown in Fig. 3, which gives the corrosion curves for turned specimens in dilute chloride solutions. The curves are apparent oxygen curves, as any hydrogen gas evolved was not estimated in these experiments.

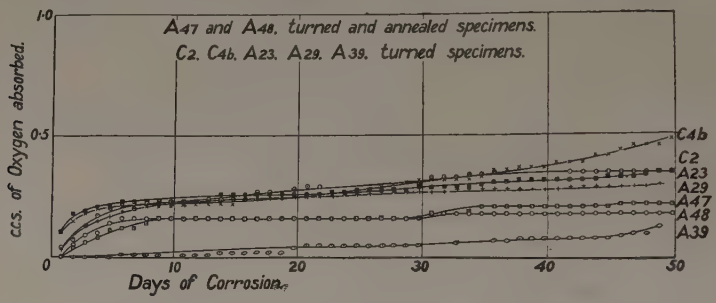

FIG. 2.—CORROSION IN CONDUCTIVITY WATER.

The hydrogen correction at these concentrations is probably small compared with the striking effect of differences in the turned surfaces. Thus both *A*40 and *A*34 were tested in N/10,000 KCl, but while corrosion stopped on *A*40 after an absorption of approximately 3.87 c.c. oxygen, *A*34 absorbed 11.18 c.c. of oxygen in a similar period. This

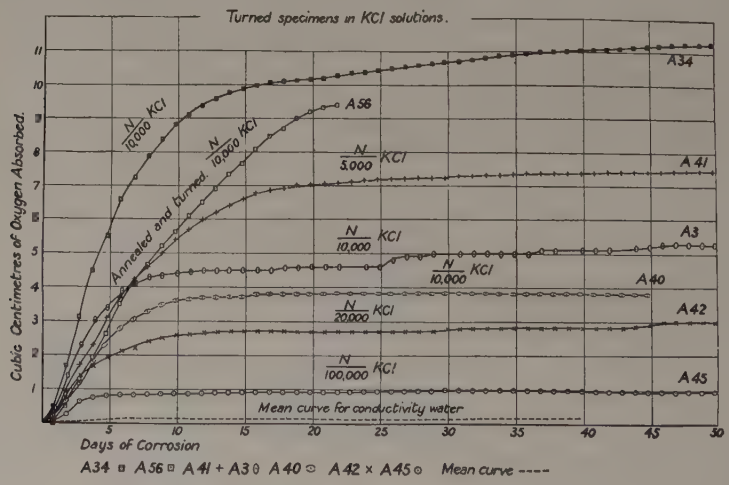

FIG. 3.—CORROSION IN DILUTE POTASSIUM CHLORIDE SOLUTIONS.

represented an increase of corrosion of 188 per cent. in *A*34 as compared with *A*40. The curve also shows that *A*34 gave considerably more corrosion than *A*41, which was tested in N/5000 KCl.

The effect of turning the surface of the metal is to produce an apparently structureless layer as viewed under the microscope, which often

shows considerable resistance to corrosion. A similar effect was shown by a specimen which was lightly burnished with an agate tool and tested in N/10,000 KCl (*A*64 in Fig. 4). Fig. 4 shows three other curves for specimens tested in N/10,000 KCl, *i. e.*, curves for a tarnished specimen (tarnished during annealing as previously described), a standard annealed specimen, and the specimen of "spectroscopically pure" zinc previously mentioned. These three specimens give results in close agreement. The effect of the tarnish film has been slight, and this may be compared with the neutral effect of the corrosion product of zinc in atmospheric corrosion as observed by Vernon.[14]

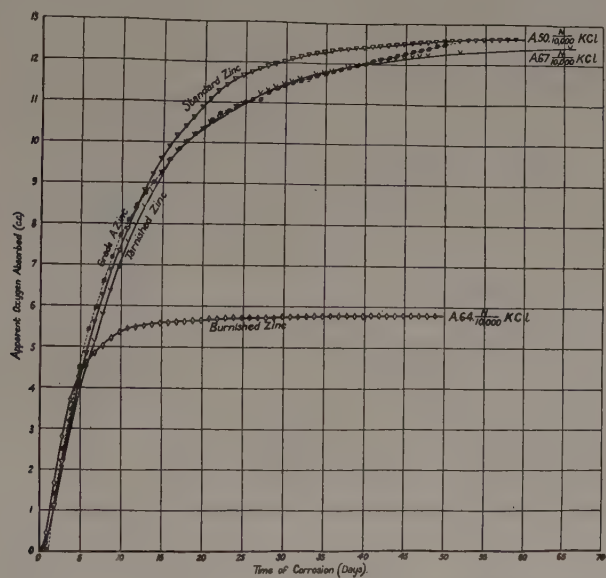

FIG. 4.—CORROSION OF STANDARD, TARNISHED, AND BURNISHED ZINC IN N/10,000 KCL.

The curves given in Fig. 4 are apparent oxygen curves, *i. e.*, curves in which hydrogen was not determined. Experiments with the electrolytic zinc showed that measurable amounts of hydrogen were evolved in tests in N/10,000 KCl. In the case of the "spectroscopically pure" zinc, a test for hydrogen was carried out at the end of the experiment. No hydrogen could be detected. Since the corrosion measured by oxygen absorption is similar to that of the less highly purified zinc, the conclusion seems to be that the higher overpotential of the purer zinc only hinders the evolution of hydrogen gas. This effect is also shown in the resistance of highly purified zinc to hydrochloric acid and sulfuric

[14] W. H. J. Vernon: Second Experimental Report to the Atmospheric Corrosion Research Committee (British Non-ferrous Metals Research Assn.): Zinc. *Trans.* Faraday Soc. (1927) **23,** 135.

acid. But electrolytic action is not wholly prevented by the absence of impurities, since corrosion proceeds normally (as in the test given above) when the hydrogen produced is removed by depolarization with oxygen.

Some typical curves obtained in N/5000 KCl solutions are given in Fig. 5, the three lowest curves being apparent oxygen curves for tests in vessels of different sizes. The lowest curve represents the result obtained in a corrosion vessel of the type most frequently used; *i. e.*, one 4.4 cm. in internal diameter and holding 100 c.c. solution (under test conditions). The others are for vessels of larger diameters, holding 500 c.c. solution.

It will be seen that the curve is concave upwards for about the first two days. Possibly this indicates the building up of the e.m.f. due to

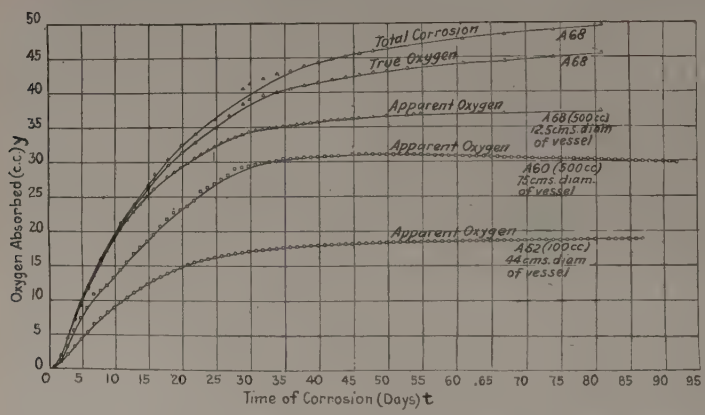

FIG. 5.—TYPICAL CURVES OBTAINED IN N/5000 KCL SOLUTIONS.

differences of oxygen concentration by the screening action of the corrosion products initially deposited.

Following this initial branch, the curves for dilute KCl solutions in many instances have been found to correspond for a considerable period to the general equation $y = A(1 - e^{-kt})$. In this equation y represents the amount of oxygen absorbed while A and k are constants.

In applying this general equation to the experimental curves, another constant b has to be introduced. This is due to the fact that the experimental curve corresponding to this equation, if produced, does not pass through the origin but only commences after a definite period. Hence the equation corresponding to the experimental curves is $y = A [1 - e^{-k(t-b)}]$.

This equation applies strictly only to true oxygen-absorption curves. The constants A and k are obtained from an experimental curve by plotting $\frac{dy}{dt}$ against y. For $\frac{dy}{dt} = k(A - y)$ so that when $\frac{dy}{dt} = 0$, $y = A$

and when $y = 0$, $\frac{dy}{dt} = kA$. Having found A and k, b can be easily found from the experimental values.

The equation has been applied to the true oxygen-absorption curve of $A68$ shown in Fig. 5. Table 1 shows the agreement between observed and calculated values.

TABLE 1.—*Observed and Calculated Values of True Oxygen-absorption Curve*

t, Days	y, Experimental	y, Calculated	t, Days	y, Experimental	y, Calculated
0.96	0.75	0.0	24	34.6	34.8
2	2.8	2.9	28	37.1	37.6
4	7.9	7.9	34	39.9	40.0
6	12.5	12.3	40	41.6	41.7
8	16.4	16.2	46	42.6	42.9
10	19.75	19.7	50	43.1	43.4
12	22.65	22.65	60	44.0	44.3
14	25.3	25.38	70	44.75	44.8
16	27.7	27.7	80	45.6	45.1
18	29.8	29.8	100	47.0	45.3
20	31.5	31.7	150	49.6	45.4

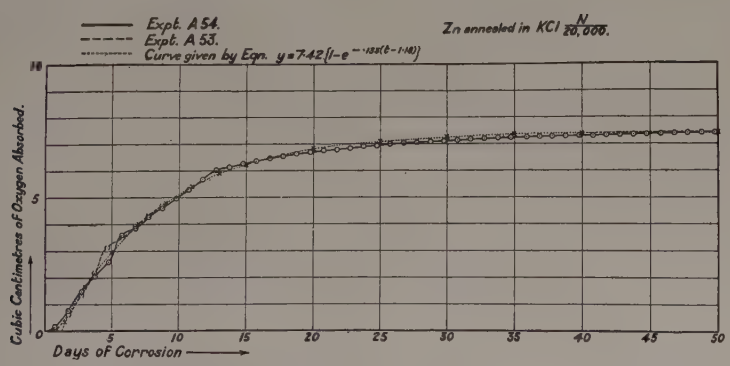

FIG. 6.—COMPARISON OF EXPERIMENTAL AND CALCULATED CURVES.

It will be seen that very good agreement is obtained for a period of about 70 days starting from the second day.

Before hydrogen measurements were taken, this equation was applied to apparent oxygen curves for solutions of N/20,000, N/10,000 and N/5000 KCl, in vessels of about 4.4 cm. dia. As will be seen from Fig. 6, very good agreement was obtained in N/20,000 KCl solution between two experimental curves and a calculated curve. The agreement between experimental and calculated values for the N/10,000 and the N/5000 KCl solutions are shown in Table 2.

TABLE 2.—*Experimental and Calculated Values for KCl Solutions*

ZN (ANNEALED) IN N/10,000 KCL

t, Days	y, Experimental	y, Calculated	t, Days	y, Experimental	y, Calculated
2	1.40	1.40	20	10.94	10.97
4	3.42	3.38	25	11.70	11.82
5	4.27	4.24	30	12.05	12.36
7	5.77	5.74	40	12.41	12.92
10	7.53	7.54	55	12.63	13.20
15	9.65	9.64	103	13.00	13.30

ZN (ANNEALED) IN N/5000 KCL

2	1.27	1.50	20	14.90	14.93
4	3.50	3.80	25	16.34	16.74
6	5.70	5.80	30	17.15	18.08
8	7.63	7.62	35	17.64	19.08
10	9.24	9.23	40	17.98	19.83
12	10.65	10.65	50	18.37	20.80
15	12.50	12.49	55	18.48	21.11

The agreement becomes less satisfactory after a period of about 20 days, this being almost certainly due to the fact that the curves were not corrected for hydrogen evolution. In the case of the N/5000 KCl it will also be noticed that the figures for the first four days do not agree well. This is due to the effect of the restriction of the rate of oxygen supply as compared with experiment *A*68, which was conducted in a much wider vessel.

The exponential curve can be deduced theoretically on certain assumptions, one of which is that the rate of diffusion of oxygen to the metal is always sufficient and does not restrict the rate of corrosion.

Other assumptions underlying the theoretical deduction of the equation for the exponential curve are:

1. That the whole process of corrosion is electrolytic.

2. That the changes in the rate of corrosion are produced only by changes in the conductivity available for corrosion currents; *e. g.*, by changes in the amount of chlorine ion in the KCl solutions. This suggests that the process is independent of polarization effects at either anode or cathode, and that the potential E which originates the corrosion currents is constant. It also suggests that the precipitated corrosion products deposited during the exponential stage of the corrosion do not affect the process. The chlorine ion is not directly removed from solution by the anodic reaction, since zinc chloride is soluble in water, but must pass into insoluble products by subsequent secondary reactions which must remove a constant proportion of the zinc chloride present at any time.

The deduction of the exponential equation is as follows. At any time t suppose:

Total quantity of electricity that has passed $= Q$
Momentary current $= i$
Effective electrolytic resistance $= r$
Let the steady e.m.f. $= E$

Let C = amount of chlorine present initially.
and C' = amount of chlorine used up at time t.
Then the amount of chlorine left $= C - C'$.

Now $$i = \frac{dQ}{dt}$$

and also $$i = \frac{E}{r}$$

At time t the electrolytic conductivity for corrosive current is proportional to the chlorine left in solution; that is

$$\frac{1}{r} = k(C - C').$$

And C' is proportional to total quantity of electricity that has passed during time t

$$\therefore C' = aQ$$

$$\therefore \frac{1}{r} = k(C - aQ)$$

$$\therefore i = \frac{E}{r} = Ek(C - aQ) = aEk\left(\frac{C}{a} - Q\right)$$

$$= K(B - Q)$$

Hence

$$\frac{dQ}{dt} = K(B - Q)$$

But if the oxygen absorbed (y) is proportional to Q then

$$\frac{dy}{dt} = K(A - y)$$

hence

$$y = A(1 - e^{-Kt})$$

It should be noted that the OH ion is not considered as available for corrosion currents in deducing the exponential, and the fact that such close agreement is obtained for a long period between the experimental and the calculated results suggests that in the conditions studied the effect of the OH ion on the true oxygen-absorption curve is small.

Effect of Restriction of Oxygen

The corrosion experiments on zinc detailed so far have been carried out in very dilute solutions. We have seen, however, that in the case of

an experiment carried out in a narrow vessel (approximately 4.4 cm.) in N/5000 solution, the curve does not agree well with the exponential for the first few days, owing to the restriction of the oxygen supply. The effect of this factor becomes more marked as the concentration of the solution is increased. This is shown in Fig. 7, which gives apparent-oxygen curves for the corrosion of zinc in KCl solutions ranging from N/10,000 to N/10, the experiments being conducted in standard-sized vessels of approximately 4.4 cm. dia. It will be seen that, after the slight initial lag, the curves for the stronger solutions are approximately straight lines which ultimately fall over into curved portions (even in the case of the N/10 solution, though this is not shown in the figure).

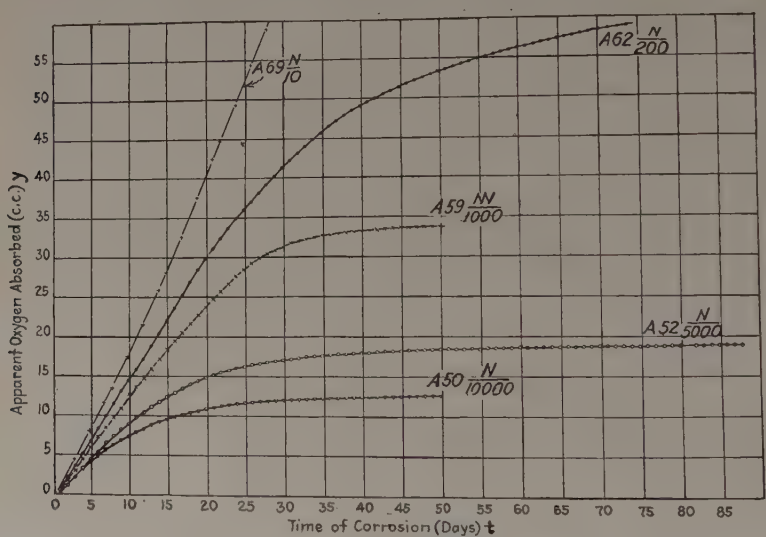

FIG. 7.—APPARENT OXYGEN CURVES FOR CORROSION OF ZINC.

It will be seen from the figure that the slopes of the curves increase with increasing concentration. This effect was unexpected, because if the rate of oxygen supply is controlling the corrosion mere variation in the concentration of the solution would not be expected to have any appreciable influence in the conditions of the experiments. The effect seems to be connected with the observation that in the stronger solutions a greater proportion of the metal surfaces, especially of the under surfaces, has become pitted. This is shown in Fig. 8. The cathodes corresponding to a few pits would probably cover only part of the metal surface, but when greater numbers of pits were present a greater proportion of the metal surface would probably be functioning as cathodes. The rate of oxygen absorption under the former conditions would be less than that under the latter.

FIG. 8.—PITTING IN RELATION TO CATHODE SURFACE.
Specimen *A*52 in N/5000 KCl; *A*59 in N/1000 KCl; *A*62 in N/200 KCl.

It is obvious that where the rate of oxygen supply is controlling the corrosion, any change in the factors which affect the rate of diffusion of oxygen through the liquid will affect the rate of corrosion.[15] Such factors are variations in the depth of the specimens, and variations in the cross-section of the liquid surfaces (unless the latter are always very large compared with the area of the specimen). The effect of increased diameter in increasing the slope can be seen by comparing the initial rates of corrosion of *A*60 and *A*68 in Fig. 5, which were both tested in 500 c.c. solution, and of *A*52, though this was tested in 100 c.c. of solution.

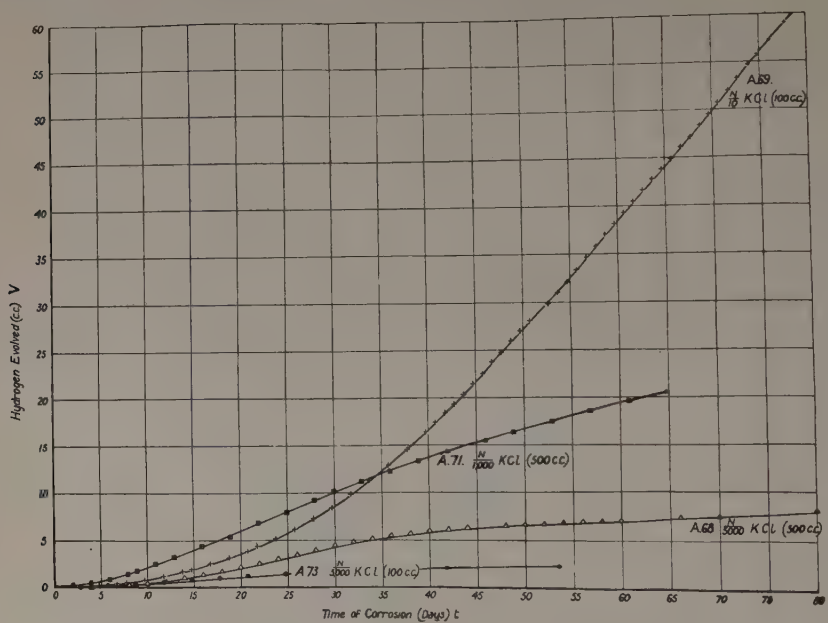

FIG. 9.—DETERMINATION OF HYDROGEN IN CORROSION TESTS.

RESULTS OF HYDROGEN MEASUREMENTS

The corrosion apparatus fitted with platinum wire, which is shown in Fig. 1, enabled the amount of hydrogen gas to be determined at intervals during the course of a test. Some of the curves obtained are given in Fig. 9. Assuming that the rate of evolution of hydrogen gas is dependent on metallic impurities of low overpotential which are liberated by the corrosion, then the amount of such impurity would be proportional to the total corrosion. As long as the deposition of impurity took place

[15] It should be noted that in the author's experiments, though convection currents due to temperature changes and evaporation are eliminated, a small convection effect still remains due apparently to change in density of the surface layer by absorption of oxygen.

only in such manner as to increase the surface area of low overpotential available for the liberation of hydrogen, the rate of hydrogen evolution at any time would be expected to be proportional to the total amount of impurity present and hence to the total corrosion at that time. Fig. 10 shows the rate of hydrogen evolution plotted against the total corrosion in the case of the test in N/10 KCl solution (*A*69). The result is in good agreement with these assumptions, as a straight line is obtained for a period of about 45 days. The curve subsequently diverges from the straight line, and, as will be seen from Fig. 9, the rate of hydrogen evolution becomes constant. However, the impurities cannot be expected to continue to spread superficially, but sooner or later will form aggregates so that the rate of hydrogen evolution does not increase proportionally.

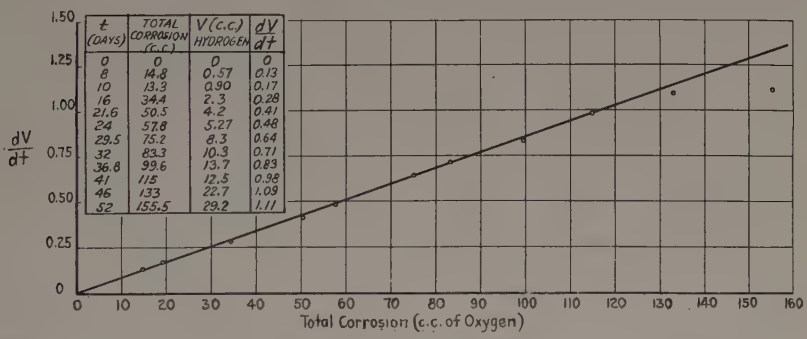

FIG. 10.—RATE OF HYDROGEN EVOLUTION PLOTTED AGAINST TOTAL CORROSION.

SUMMARY

Some of the principal results of the investigations described here, and in greater detail in the papers to which reference has been made, may be summarized as follows:

1. Quantitative measurements of considerable accuracy accord well with the view that the main action of the corrosion of zinc in KCl solutions is electrochemical in character, since the equations characteristic of the experimental curves are identical in form with those derived from electrochemical considerations based on certain simple and reasonable assumptions.

2. Corrosion-time curves have been obtained for zinc in conductivity water and potassium chloride solutions exposed to oxygen gas at a pressure of 760 mm. The corrosion in conductivity water is very small in comparison with that which occurs even in very dilute KCl solutions.

3. After a short initial period, the oxygen-absorption curves obtained for potassium chloride solutions are generally as follows:

a. In dilute potassium chloride solutions (N/5000 or weaker) curves are obtained of the exponential form $y = A(1 - e^{-kt})$. Such curves are obtained when the oxygen reaching the metal is amply sufficient for

corrosion and the gradual decrease in the rate of corrosion is produced by the decrease in the concentration of chlorine ions.

b. In stronger KCl solutions the curves are approximately straight line, which ultimately fall over into curves becoming parallel to the time axis. The straight line portions of the curves may last for as much as 100 days in 100 c.c. of N/10 KCl solution. During this period the rate of oxygen supply to the metal is the controlling factor. With increasing concentration of KCl the slopes of the straight lines increase even in similar vessels, up to a maximum at a concentration less than N.

4. Under the test conditions hydrogen gas is liberated during the corrosion of zinc in KCl solutions of concentration N/10,000 or stronger except when the "spectroscopically pure" zinc is used. The evolution of the gas can be explained by assuming that impurities of low overpotential are set free by the primary corrosion. In the case of N/10 KCl solution the rate of hydrogen evolution has been shown to be proportional to the total corrosion for a considerable period; its amount may reach 14 per cent. of the total corrosion.

5. The treatment of the surface of the metal affects the curves considerably. Turned specimens may give very different results under similar conditions and usually corrode less than annealed specimens. To obtain consistent results it has been found necessary to anneal the zinc specimens at about 260° C.

Acknowledgment

This research has been directed by the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research. The thanks of the authors are due to Prof. G. T. Morgan, Director of the Chemical Research Laboratory, for the many facilities afforded for their work. A number of the figures were taken from the authors' paper read before the Royal Society, mentioned on page 33.

Some Aspects of Corrosion-fatigue

By T. S. Fuller,* Schenectady, N. Y.

(New York Meeting, February, 1929)

The work of D. J. McAdam, Jr.[1,2] at the U. S. Naval Engineering Experiment Station, Annapolis, Md., on what has been called by him "corrosion-fatigue" has focussed the attention of the engineering profession in general, and of those interested especially in the study of corrosion in particular, on the importance of making tests which will indicate as nearly as possible what can be expected from a given material in service. Pitting is unquestionably the chief agent operating so tremendously to reduce fatigue limits, but in the light of previous work[3, 4, 5, 6, 7, 8] it is fair to assume that absorbed hydrogen resulting from the action of the corroding medium upon steel may, under certain conditions, have a perceptible influence.

The experiments described in this paper deal more precisely with stressless corrosion, or "prior-corrosion fatigue,"[9] and have been carried out to test such an assumption, to segregate, if possible, the effect of pitting from that of absorbed hydrogen, and although very preliminary in nature they indicate results which are striking.

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* Research Laboratory, General Electric Co.

[1] D. J. McAdam, Jr.: Stress-strain-cycle Relationship and Corrosion-fatigue of Metals. *Proc.* Am. Soc. Test. Mat. (1926) **26,** 224; Corrosion-fatigue of Metals as Affected by Chemical Composition, Heat-treatment and Cold Working. *Trans.* Am. Soc. Steel Treating (1927) **11,** 355; Corrosion-fatigue of Non-ferrous Metals. *Proc.* Am. Soc. Test. Mat. (1927) **27,** Pt. 2; Fatigue, and Corrosion-fatigue of Metals. *Proc.* Internat. Congress for Testing Materials, Amsterdam, Sept. 1927.

[2] D. J. McAdam, Jr.: Corrosion of Metals as Affected by Time and Cyclic Stress. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 571.

[3] G. Charpy and S. Bonnerot: On the Permeability of Iron for Hydrogen. *Compt. Rend.* (1912) **154,** 592.

[4] G. Charpy and S. Bonnerot: On the Reactions which Accompany the Osmosis of Hydrogen through Iron. *Compt. Rend.* (1913) **156,** 394.

[5] J. Coulson: The Electrolytic Pickling Process and Its Effect on the Physical Properties of Iron and Steel. *Trans.* Am. Electrochem. Soc. (1917) **32,** 237.

[6] P. D. Merica: The Embrittling Action of Sodium Hydroxide on Mild Steel, and Its Possible Relation to Seam Failures of Boiler Plate. *Met. Chem. Eng.* (1917) **16,** 496.

[7] T. S. Fuller: The Prevention of Brittleness in Electroplated Steel Springs. *Trans.* Am. Electrochem. Soc. (1917) **32,** 247.

[8] T. S. Fuller: The Penetration of Iron by Hydrogen. *Trans.* Am. Electrochem. Soc. (1919) **36,** 113.

[9] D. J. McAdam, Jr.: *Op. cit., Proc.* Inst. Metals Div., A. I. M. E. (1928).

Apparatus and Test Specimens

The Farmer type of rotating beam testing machine for reversed bending, operating at a speed of 1800 r.p.m., was used. The material tested was 3½ per cent. nickel steel containing 0.35 per cent. carbon, oil-quenched from 825° C., and drawn back to 600° C. The static physical properties of a representative sample were:

Ultimate strength, 110,000 lb. per sq. in.
Yield point, 80,000 lb. per sq. in.
Proportional limit, 75,000 lb. per sq. in.
Percentage elong. in 2 in., 24.
Percentage reduction of area, 55.

The test specimens were similar to those described by Moore and Jasper,[10] being 13 in. in length and 0.400 in dia., except at the reduced section in the center, the minimum diameter of which was 0.270 in. cut on a 9⅞-in. radius. Specimens were machined with great care, special precautions being taken to remove the metal a little at a time in very light cuts to avoid disturbing the structure underneath the surface. The reduced section was polished with 00 emery. In this set of experiments no attempt has been made to determine endurance limits. All tests have been carried out at a maximum stress of 90,000 lb. per sq. in., and the numbers of cycles required to fracture the specimens, treated in different ways, have been compared. The writer is aware that such a method of comparison does not meet with the approval of those skilled in the art of fatigue testing, and therefore begs the reader to bear in mind the preliminary nature of this report.

Uncorroded Specimens

Four uncorroded specimens, Nos. 1, 2, 3 and 4, Table 1, fractured at 105,300, 107,100, 127,700 and 140,900 cycles (see Fig. 7).

Specimens Pickled in 10 *Per Cent. Sulfuric Acid*

Four specimens, 5, 6, 7 and 8, were pickled 1 hr. in 10 per cent. sulfuric acid; 5 and 6 were tested immediately after removal from the bath and 7 and 8 were heated 4 hr. at 130° C. to remove absorbed hydrogen, and tested. The former fractured at 62,000 and 66,500, and the latter at 74,400 and 76,900 cycles, respectively. (Fig. 7.) The four samples were pickled at the same time and in the same acid. It is therefore reasonable to suppose that each suffered pitting to the same extent, and that the slightly better life shown by specimens 7 and 8 was due to the removal of absorbed hydrogen from these samples. Fig. 1

[10] H. F. Moore and T. M. Jasper: An Investigation of the Fatigue of Metals. Univ. Illinois *Bull.* 136 (May, 1923) 96.

shows a section of the longitudinal surface of specimen 6 at a point adjacent to the fracture.

As Cathode in 5 Per Cent. NaOH Solution

To determine the effect of absorbed hydrogen in the absence of pitting, specimens 9 and 10 were made the cathode in 5 per cent. NaOH solution, specimen 9 for 24 hr. and 10 for 48 hr. The anode was platinum. Both specimens were tested immediately upon removal from the solution, 9 requiring 78,100 and 10 82,400 cycles to fracture. (Fig. 7.) The inferior life of these samples can be logically attributed to nascent hydrogen.

Effect of Schenectady Tap Water

Four specimens, 11, 12, 13 and 14, were kept for 1 week in a glass dish through which tap water was flowing. Specimens 11 and 12 were broken immediately after removal from the water and required 51,000 and 35,700 cycles to fracture. Specimens 13 and 14 were tested after heating 4 hr. at 130° C. to remove hydrogen, if present. It required 41,300 and 38,100 cycles, respectively, to fracture these specimens. (Fig. 7.) The fact that the four specimens gave similar results, regardless of whether or not the low temperature anneal was applied, indicates that hydrogen is not a factor in the loss of fatigue life sustained by ferrous materials during water corrosion at room temperature.

A study of the surface, adjacent to the fracture, of the water-corroded specimens is interesting. McAdam[11] has pointed out that the loss in fatigue strength of samples treated in this manner is due to stress concentration at the rather deep pits formed with this type of corrosion. The way in which fracture occurs through the pits is well illustrated by Fig. 2 which is an etched portion of the longitudinal section of the surface of specimen 11 adjacent to the fracture. The nature of the unetched surface, adjacent to the fracture, of the other half of specimen 11, is shown by Fig. 3. As in Fig. 2 cracks are to be seen extending from certain of the pits.

It is further interesting to note that an exposure of 1 week to Schenectady tap water is far more injurious than 1 hr. in a solution of 10 per cent. sulfuric acid.

Protective Coatings

To prevent the pitting shown in Figs. 2 and 3, two specimens, 15 and 16, were hot-galvanized, and two others, 17 and 18, were dipped in molten tin after which all four were exposed to running tap water for 1 week. At the end of the corrosion period, no porosity of either coating was

[11] D. J. McAdam, Jr.: *Op. cit.*, *Proc.* Inst. Metals Div., A. I. M. E. (1928).

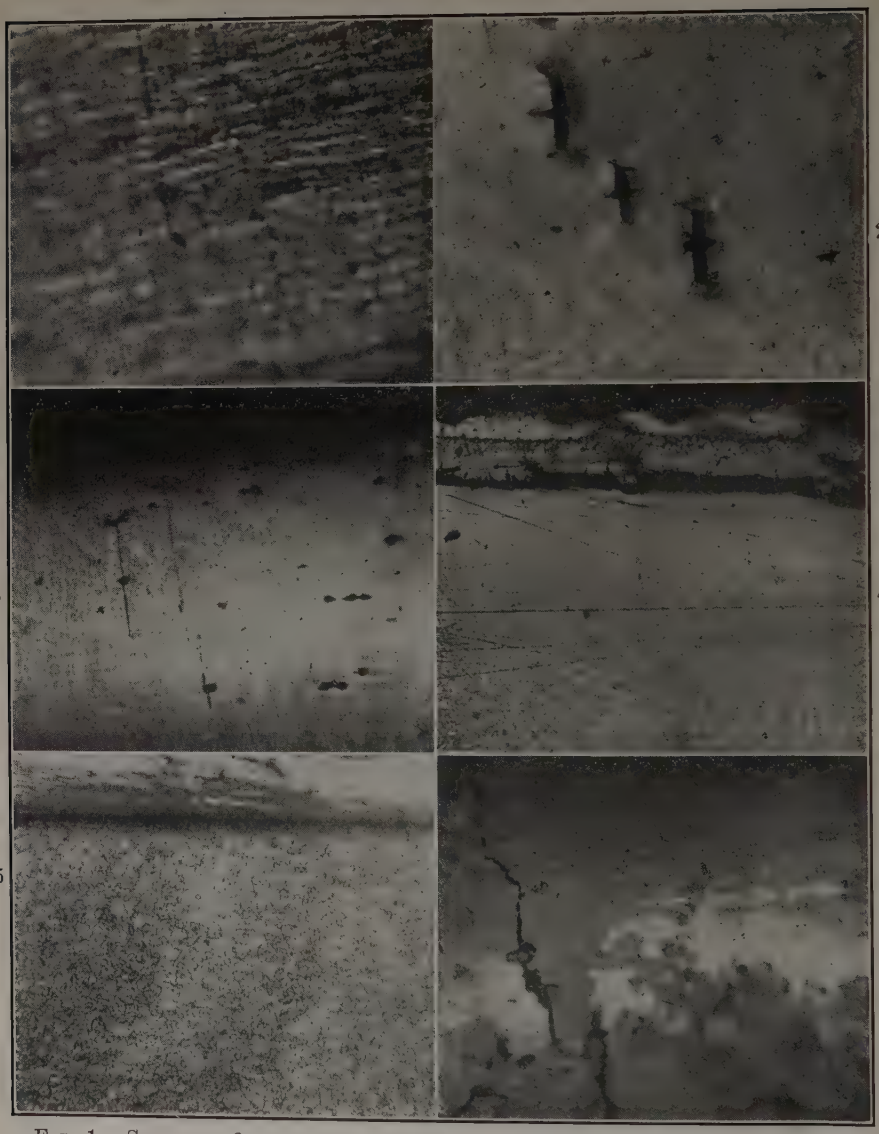

FIG. 1.—SPECIMEN 6; PORTION OF SURFACE ADJACENT TO FRACTURE. × 20.

FIG. 2.—SPECIMEN 11; PORTION OF SURFACE ADJACENT TO FRACTURE. ETCHED WITH A SOLUTION OF NITRIC AND ACETIC ACIDS. × 20.

FIG. 3.—SPECIMEN 11; PORTION OF SURFACE ADJACENT TO FRACTURE. UNETCHED. × 20.

FIG. 4.—SPECIMEN 15; LONGITUDINAL SECTION NEAR FRACTURE, SHOWING ZINC AND BASE METAL. ETCHED WITH 5 PER CENT. HNO_3 IN ALCOHOL. × 100.

FIG. 5.—SPECIMEN 18; LONGITUDINAL SECTION NEAR FRACTURE, SHOWING TIN AND BASE METAL. ETCHED WITH 5 PER CENT. HNO_3 IN ALCOHOL. × 100.

FIG. 6.—SPECIMEN 19; PORTION OF SURFACE ADJACENT TO FRACTURE. × 20.

indicated by the ferroxyl test.[12] When tested for fatigue, however, specimens 15 and 16 failed respectively at 50,500 and 34,300, and 17 and 18 at 178,800 and 140,900 cycles. (Fig. 7.) The zinc and tin were equally effective over the period of 1 week in preventing pit formation.

The reason for the inferior life of the zinc-coated specimens is disclosed by Fig. 4, which is a longitudinal section of specimen 15 at a point near the fracture showing zinc coating and base metal. Hair line cracks beginning at the junction of zinc and base metal, originating probably in the $FeZn_3$ layer, and extending into the base metal, can be seen. No such condition exists in the tin-coated specimens as evidenced by Fig. 5, which shows a similar section of tin-coated specimen 18.

Corrosion by Steam

Specimens 19 and 20, which were immersed 1 month in an atmosphere of 100° C. steam and air, at atmospheric pressure, and tested 72 hr. after removal from the bath, required 27,400 and 34,400 cycles to fracture. (Fig. 7.) As in the case of samples corroded by tap water, the cracks followed corrosion pits as shown by Fig. 6, which is a reproduction of a portion of the surface adjacent to the fracture.

Table 1.—*Stressless Corrosion Tests on Nickel Steel*

[Maximum Stress = 90,000 lb. per sq. in.]

Specimen No.	Treatment of Specimen	Number of Cycles Required to Fracture
1	Uncorroded	105,300
2	Uncorroded	107,100
3	Uncorroded	127,700
4	Uncorroded	140,900
5	Pickled 1 hr. in 10 per cent. H_2SO_4; tested immediately	62,000
6	Pickled 1 hr. in 10 per cent. H_2SO_4; tested immediately	66,500
7	Pickled 1 hr. in 10 per cent. H_2SO_4; heated 4 hr. at 130° C.	74,400
8	Pickled 1 hr. in 10 per cent. H_2SO_4; heated 4 hr. at 130° C.	76,800
9	Cathode 24 hr. in 5 per cent. NaOH solution	78,100
10	Cathode 48 hr. in 5 per cent. NaOH solution	82,400
11	Immersed 1 week in running tap water; tested immediately	51,000
12	Immersed 1 week in running tap water; tested immediately	35,700
13	Immersed 1 week in running tap water; heated 4 hr. at 130° C.	41,300
14	Immersed 1 week in running tap water; heated 4 hr. at 130° C.	38,100
15	Hot-galvanized; 1 week in running tap water	30,300
16	Hot-galvanized; 1 week in running tap water	34,300
17	Tin-dipped; 1 week in running tap water	178,800
18	Tin-dipped; 1 week in running tap water	140,900
19	Immersed 1 month in steam + air	27,400
20	Immersed 1 month in steam + air	34,400

[12] K. Pitschner: A Rapid and Practical Method of Applying the Ferroxyl Test to Protective Coatings. *Proc.* Am. Soc. Test. Mat. (1927) **27**, 304.

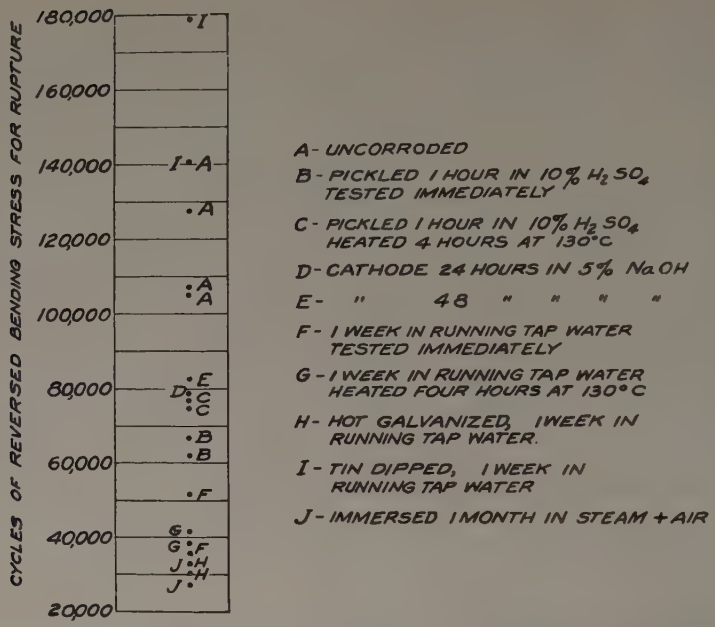

FIG. 7.—CHART SHOWING NUMBER OF CYCLES OF REVERSED BENDING STRESS FOR RUPTURE AFTER VARIOUS TREATMENTS; MAXIMUM STRESS IN ALL TESTS 90,000 LB. PER SQ. IN.

CONCLUSIONS

The experiments are in accord with the assumption that absorbed hydrogen is a factor contributing to the loss in fatigue strength exhibited by ferrous materials after certain types of corrosion. Of four specimens pickled 1 hr. in 10 per cent. sulfuric acid, two which were heated 4 hr. at 130° C. to remove hydrogen, showed an average "life" 18 per cent. greater than those pickled, but not heated. Two specimens made cathode in 5 per cent. sodium hydroxide exhibited no pitting, but showed an average "life" 33 per cent. less than that of the uncorroded specimens.

Serious pitting which caused a loss of 65 per cent. in the number of cycles required to fracture, resulted from an exposure of 1 week in tap water. The tap water samples which were treated to remove hydrogen, if present, showed the same results as those tested immediately after removal from the water, indicating that hydrogen is not a factor in this type of corrosion.

Tin-dipped specimens, subjected to tap water corrosion for 1 week, showed an average "life" equal to that of uncorroded specimens. Hot-galvanized specimens, similarly treated, showed an average loss of 73 per cent. in the number of cycles required to fracture, due probably to the brittle character of the bond between steel and zinc coating.

Specimens immersed in a mixture of wet steam and air for one month showed an average loss of 74 per cent. in the number of cycles required to fracture.

DISCUSSION

[Includes also discussion of paper by D. J. McAdam, Jr., which begins on page 56.]

H. F. Moore, Urbana, Ill. (written discussion).—The experiments described by Mr. Fuller seem to have been chosen to bring out the effect of a number of interesting conditions tending to cause corrosion. Mr. Fuller himself notes that the method he used for evaluating endurance under repeated stress is not an approved method. He used a standard stress of about 80 per cent. of the static ultimate tensile strength. Under these conditions the changes in *ductility* introduced by the various chemical treatments would play a large part in the results, probably fully as large a part as would the fatigue *strength*. It is not altogether certain that if tests had been run at a lower standard stress the different treatments would have been arranged in the same order as regards damage done. It is to be hoped that further experiments can be run in which lower stresses are used and in which some attempts can be made to determine endurance limit, in order to check qualitatively as well as quantitatively the significance of Mr. Fuller's results.

F. N. Speller, Pittsburgh, Pa.—Mr. Fuller's preliminary tests on the influence of absorbed hydrogen are suggestive, but it is understood, of course, that he does not intend to draw definite conclusions at this time.

The tests made with caustic soda do not show a decrease in endurance limit with time of stressless corrosion. The results would be more conclusive if some of the samples had been heated before testing to remove hydrogen. More data on pickling and the treatment of the zinc-coated and tin-coated samples would be useful.

In making further experiments it would seem desirable to include a steel that is more susceptible to hydrogen embrittlement than the nickel steel used in these tests.

In discussing Dr. McAdam's A. S. T. M. paper in 1926, the possible influence of hydrogen on corrosion under stress was suggested, but I had in mind at that time the possible relation between the so-called "caustic embrittlement" of steel at steam-boiler temperatures and corrosion fatigue, the effect of hydrogen in this connection apparently being to weaken the bond between the grains by reduction of oxide inclusions.

Dr. McAdam has again placed us under great obligation for the masterly way in which he has obtained and presented new data on the effect of time and stress cycles on corrosion-fatigue. It is to be regretted, however, that he has not seen fit to summarize his conclusions in brief form, as no one is so well able to do this as Dr. McAdam. However, the separate effect of each of these factors will be seen after a careful study of the various graphs.

Dr. McAdam is quite correct in saying that these graphs require and deserve very careful study. At the same time I do not see why he should not state tentatively his conclusions, rather than wait until the work has been finished.

The striking reduction in fatigue limit by "corrosion-stress" in brackish water compared with tests in fresh water, as shown in Fig. 1, is significant and suggestive of the use that can be made of corrosion-fatigue as a measure of the film-building rate in various solutions.

Static corrosion tests would be useful for comparison in these waters, but in the absence of better data the A. S. T. M. immersion tests in this brackish water (one-sixth sea water) and in fresh tap water (of Washington, D. C.) show the former to be less

corrosive, and suggest that the opposite results obtained under corrosion-stress are probably due to the inability of the brackish water to repair the protective surface film when the metal is under rapidly alternating stress.

We have shown that the reduction in fatigue limit may be prevented by adding sodium dichromate to the water, to increase the film-building power of the water. The amount of passifier required depends on the composition of the water, but in some cases (where the chloride contents are very high, for example) the destructive effect of the stress and other factors cannot be entirely neutralized.

However corrosion is studied, one is fairly sure to find that it leads to a study of metal surface film equilibrium. The resultant of the various forces which either tend to build up or to destroy these films determines the ultimate damage to the metal.

The rapidity with which a passive film is reformed is indicated by the fact that 200 p.p.m. sodium dichromate in tap water is sufficient to give complete protection under corrosion-stresses at 1400 r.p.m., although immersion for several hours in this solution without stress will not materially prolong the life of the metal when later exposed under corrosion-stress in the same water without the inhibitor.

This method also enables measurements to be made of the destructive effect of concentration cells and other localized corrosion on protective films, but that is another story.

D. J. McAdam, Jr.—The object of my investigation was to study quantitative relationships between four variables. These relationships are represented in the paper by the diagrams. The diagrams, therefore, are the conclusions.

Mr. Fuller's paper serves a useful purpose in drawing attention to the possibility that at least part of the damage caused by corrosion is due to weakening of the metal by absorption of a foreign substance. In my own papers on corrosion of metals under cyclic stress I have emphasized the damaging effect of stress concentration at the bottoms of corrosion pits. Nevertheless there is the possibility that part of the effect of corrosion in lowering the fatigue limit may be due to weakening of the metal by absorption of a foreign substance. I believe, however, that no convincing evidence has yet been presented that such possible weakening of the metal is due to hydrogen. It seems more probable that weakening may be due to absorption of oxygen in the surface layer of metal.

I am inclined to agree with Mr. Fuller that the effect of hydrogen is negligible in lowering the fatigue limit of metals in contact with water. It does not seem, however, that he has yet proved that hydrogen causes damage under corrosion in contact with sulfuric acid or alkali. I should like to illustrate this by a diagram.

In investigation of fatigue we do not get a correct perspective unless we consider the entire stress-cycle graph. This is illustrated by Fig. 8, in which graphs are plotted on a semilogarithmic scale. Mr. Fuller's experiments are represented by the graphs at an ordinate of 90,000. The ranges of number of cycles required to cause failure are represented by the widths of the various graphs. As shown in his paper, the range of number of cycles for his four specimens tested in air is about 34 per cent. (If the two zinc-coated specimens, which endured a greater number of cycles, are included, the range for the entire six specimens is 70 per cent.) This range seems very large, but when the graph is extended down toward a horizontal asymptote, as shown in the figure, the range of fatigue limits is only about 5 per cent.

For the specimens tested in sulfuric acid, the range of numbers of cycles is only 24 per cent. For specimens tested in water the extreme range is about 42 per cent. These percentage ranges, therefore, are of about the same order as for the four specimens tested in air. There is no more evidence presented that hydrogen is an important cause of damage by sulfuric acid than of damage by water.

Mr. Fuller shows that caustic soda lowers the fatigue limit, but comparison tests are needed with specimens that have been treated with caustic soda and then treated for removal of hydrogen before determining the fatigue limit.

I do not believe, therefore, that time is saved by making tests at stresses far above the fatigue limit and comparing numbers of cycles. A much better method is to make the fatigue tests for corroded steel at stresses that will cause failure between 1,000,000 and 10,000,000 cycles. For each test, the fatigue limit may then be approximately determined by drawing a curve parallel to the ordinary fatigue graph.

Mr. Fuller has some excellently planned experiments under way. These should lead to results of great value.

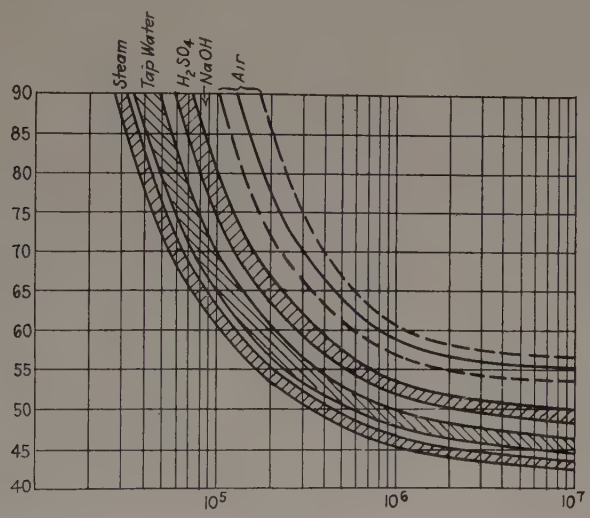

Fig. 8.

T. S. Fuller.—With respect to Professor Moore's discussion, it has been very definitely pointed out in the paper that it has been recognized that the method of comparing results obtained at a single stress does not meet with the approval of those skilled in the art of fatigue testing, and for this reason that this paper must be considered to be of a preliminary nature.

I agree with Mr. Speller that the experiments with caustic soda and sulfuric acid would have been more conclusive had other specimens similarly treated been heated to remove absorbed hydrogen and subsequently tested.

Dr. McAdam referred to the possible effect of the absorption of hydrogen in surface film of steel. Such an effect is not necessarily confined to the surface, for the reason that hydrogen is known to diffuse quite rapidly through iron at room temperature.

Dr. McAdam is of the opinion that the loss in fatigue life of specimens exposed to sulfuric acid and sodium hydrate has not been proved to be due to absorbed hydrogen. Perhaps this is true. It is, however, apparent that the terms "reasonable to suppose" and "logically attributed," used in the paper are justified by the evidence offered.

Corrosion of Metals as Affected by Stress, Time, and Number of Cycles*

By D. J. McAdam, Jr.,† Annapolis, Md.

(New York Meeting, February, 1929)

Part I—Outline of Investigation, Description of Material and Methods

Previous Investigation of Corrosion-fatigue

Results of investigation of corrosion-fatigue of metals at the U. S. Naval Engineering Experiment Station have been presented by the author in four papers.[1,2,3,4] In those papers references were given to the work of Haigh in 1917.[5] The investigation at Annapolis included a variety of ferrous and non-ferrous alloys. The experiments showed that even slight corrosion simultaneous with fatigue may cause failure at stresses far below the ordinary endurance limit. The experiments also showed that, for most metals, severe stressless corrosion prior to fatigue is much less damaging than even slight corrosion simultaneous with fatigue. The term "corrosion-fatigue" was restricted to mean the simultaneous action of corrosion and fatigue. The combined effect of corrosion followed by fatigue was called "prior-corrosion fatigue."

A stress-cycle graph representing corrosion-fatigue is a curve approaching a horizontal asymptote, the ordinate of which may be called a "corrosion-fatigue limit." To avoid confusion in later discussion, the term "endurance limit" will be restricted to mean the fatigue limit obtained by tests in air with specimens as free as possible from stress concentration and from corrosion. The endurance limit as thus obtained presumably represents an inherent property of the metal.

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* Published by permission of the Secretary of the Navy.

† Metallurgist, U. S. Naval Engineering Experiment Station.

[1] D. J. McAdam, Jr.: Stress-strain-cycle Relationship and Corrosion-fatigue of Metals. *Proc.* Am. Soc. Test. Mats. (1926) **26**, Pt. II, 224.

[2] D. J. McAdam, Jr.: Corrosion-fatigue of Metals as Affected by Chemical Composition, Heat Treatment and Cold Working. *Trans.* Am. Soc. Steel Treat. (1927) **11**.

[3] D. J. McAdam, Jr.: Corrosion-fatigue of Non-ferrous Metals. *Proc.* Am. Soc. Test. Mats. (1927) **27**, Pt. II, 102.

[4] D. J. McAdam, Jr.: Fatigue and Corrosion-fatigue of Metals. Presented at International Congress for Testing Mats., Amsterdam, September, 1927, and published in the Congress *Proceedings*.

[5] B. P. Haigh: Experiments on the Fatigue of Brasses. *Jnl.* Inst. Metals (1917) **55**.

A tentative analysis of the corrosion-fatigue process was given by the author in his paper presented at the International Congress for Testing Materials. According to this analysis, if the initial stress is below the endurance limit but above the corrosion-fatigue limit, the corrosion-fatigue process is divided into two periods. The first period is the formation of pits. As the initial stress is below the endurance limit, such pit formation is assumed to be due to electrolytic solution pressure, not to ordinary fatigue. The electrolytic solution pressure that causes the pitting, however, is possibly not the solution pressure of stressless corrosion, but an enhanced solution pressure due to the cyclic stress. Whatever may be the reason, a metal under cyclic stress behaves as if the solution pressure were increased by the cyclic stress.

As the pit progresses, both the actual stress and the effective solution pressure increase. The increase of actual stress is due to the stress concentration at the bottoms of the pits. The increase of effective solution pressure is due to the increase of actual stress.

The mutual intensification of stress and solution pressure continues until the actual stress at the bottoms of the pits surpasses the endurance limit. The second period of corrosion-fatigue then begins. In this period the process is merely fatigue accelerated by the corrosion. The cracks advance at a continually accelerated rate until the specimen breaks.

Previous Investigation of Effect of Cyclic Stress on Corrosion

According to this analysis of the corrosion-fatigue process, the depth and sharpness of the pits formed in the first period of corrosion-fatigue depend not only on the natural susceptibility of the alloy to corrosion pitting, but also on the influence of cyclic stress on corrosion pitting. Knowledge of the effect of cyclic stress on corrosion pitting, therefore, is necessary for an understanding of corrosion-fatigue. As very little was known about the effect of cyclic stress on corrosion, an investigation of this subject was started at the Naval Engineering Experiment Station. Some results of the investigation were presented in two papers.[6,7] These results have not only thrown light on the corrosion-fatigue process but have made it possible to view the corrosion-fatigue process as part of a broad subject, the influence of stress, time and number of cycles on corrosion.

These two papers discussed the effect of cyclic stress on corrosion of a number of ferrous and non-ferrous metals. The effect of corrosion under cyclic stress was estimated by observing the resultant change in the fatigue limit. The fatigue limit of the previously corroded specimen was

[6] D. J. McAdam, Jr.: Corrosion of Metals as Affected by Time and by Cyclic Stress. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 571.

[7] D. J. McAdam, Jr.: Some Factors Involved in Corrosion and Corrosion-fatigue of Metals. *Proc.* Am. Soc. Test. Mats. (1928) **28,** Pt. II.

compared with the endurance limit of the alloy. For this purpose, specimens were subjected to corrosion at various cyclic stresses from zero to the corrosion-fatigue limit, for various times, and at various cycle frequencies. The specimens were then oiled and subjected to fatigue test at 1450 r.p.m. in air. Each experiment, therefore, consisted of two stages, a corrosion stage and a fatigue stage. The lowering of the fatigue limit due to the corrosion was used as a criterion of the depth and sharpness of the corrosion pitting.

Results of the stage 2 fatigue tests were presented in ordinary stress-cycle graphs. From the fatigue limits obtained by means of these type 1 graphs, several other types of graphs were derived to illustrate the effect of cyclic stress, time, and number of cycles.

Outline of Continued Investigation of Effect of Cyclic Stress on Corrosion

As shown in the two papers just mentioned, penetration of metal under corrosion depends on three variables (in addition to others): stress, time, and number of cycles. The object of the investigation described in the present paper was to study further the effect of these three variables on the fatigue limit. The interrelationship of four variables, therefore, is to be considered.

In investigating this subject the method of experiment was that described in the two previous papers.[6,7] Each experiment consisted of two stages. In the first or corrosion stage the specimen was subjected to cyclic stress while in contact with water. In the second or fatigue stage, the corroded specimen, after being oiled, was subjected to fatigue test at 1450 r.p.m. in air.

The term "corrosion-stress" will be used to designate the cyclic stress used in the first or corrosion stage. The term "fatigue limit" or "resultant fatigue limit" will be used to designate the fatigue limit as obtained by stage 2 tests.

The interrelationship of corrosion-stress, time, number of cycles, and fatigue limit, is illustrated in the paper by graphs of various types. Some of these types were used in the two previous papers last mentioned. Seven additional types, however, have been developed. Three-dimensional representation of the stress-time-cycle relationship has also been discussed.

Machines and Specimens

The rotating cantilever machines and specimens have been described in previous papers.[8,9] The conically tapered specimen is so designed that

[6,7] Frequent reference is made to these two papers, therefore the footnote is not repeated. The complete references are given near the beginning of this paper.

[8] D. J. McAdam, Jr.: Endurance of Steels under Repeated Stress. *Chem. & Met. Eng.* (1921) **25**, 1081.

[9] D. J. McAdam, Jr.: Endurance Properties of Steel: Their Relation to Other Physical Properties and to Chemical Composition. *Proc.* Amer. Soc. Test. Mats. (1923) **23**, Pt. II, 56.

the maximum stress is ¾ in. out from the inner fillet, and the stress varies only about 1.5 per cent. over a length of 1.5 in. With this specimen, therefore, a comparatively large region may be subjected to simultaneous corrosion and cyclic stress.

The method of alternate longitudinal and transverse polishing of specimens has been previously described.[9,10] The surface finish by this method is sufficiently smooth to permit examination of the structure at a magnification of 100. Details of machining and polishing are tabulated and kept on file at the Naval Engineering Experiment Station. This information is available for those who are interested.

The Corrosion Stage

In the corrosion stage, the specimens described, while under cyclic stress, were corroded in a water stream, which was diagonally applied so as to surround with water the tapered portion of the specimen. Specimens were thus corroded under various stresses and cycle frequencies, for various times and numbers of cycles.

In these experiments two kinds of water were used, the carbonate water and the Severn River water that were used in experiments described in previous papers.[2,3,4,7] In Severn River water the salt content averages about one-sixth that of sea water.

Material, Chemical Composition and Heat Treatment

Material for this investigation was obtained in the form of round rods ⅞ or 1 in. dia. The chemical composition of the alloys used is given in Table 1. Details of heat treatment are given in Table 2.

TABLE 1.—*Chemical Composition of Material*

All Values are Averages of at Least Two Determinations, Usually More

Material	Designation	Carbon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.	Silicon, Per Cent.	Nickel, Per Cent.	Chromium, Per Cent.
Ingot iron	IZ	0.018	0.016	0.005	0.031	0.002		
0.24 per cent. carbon steel	IH	0.24	0.57	0.005	0.036	0.006		
High-carbon steel	EM	1.09	0.33	0.023	0.015	0.28		
Silicon-nickel steel	HG	0.47	0.87	0.013	0.015	1.58	3.11	0.32
Nickel steel	IW	0.28	0.50	0.015	0.036	0.19	3.70	0.26
Chromium-nickel steel	BC	0.28	0.69	0.014	0.016	0.21	1.51	0.73
Chromium-nickel steel	AY	0.43	0.60	0.023	0.016	0.21	2.16	0.95

[10] D. J. McAdam, Jr.: Endurance Properties of Alloys of Nickel and of Copper. *Trans.* Amer. Soc. Steel Treat. (1925) **7**, 54, 217, 281.

TABLE 2.—*Heat Treatments of Material*

Material	Designation	Heated to — Deg. F.	Time Held, Min.	Cooled in	Re-heated to — Deg. F.	Time Held, Min.	Cooled in
Ingot iron	IZ-17.5	1750	45	Furnace			
0.24 per cent. carbon steel	IH-W-9	1650	60	Water	900	120	Air
0.24 per cent. carbon steel	IH-16.5	1650	60	Furnace			
High-carbon steel	EM-14.75	1475	60	Furnace			
Nickel steel	IW-W-9	1450[a]	60	Water	900	120	Furnace
Nickel steel	IW-W-10	1450[a]	60	Water	1000	120	Furnace
Nickel steel	IW-W-11	1450[a]	60	Water	1100	120	Furnace
Nickel steel	IW-14.5	1450	60	Furnace			
Silicon-nickel steel	HG-O-7.5	1500	60	Oil	750	60	Air
Chromium-nickel steel	BC-W-10	1550	60	Water	1000	120	Furnace
Chromium-nickel steel	AY-W-10	1500	60	Water	1000	120	Furnace

[a] Previously heated to 1675° F., held 60 min., cooled in air.

Tension and Impact Tests

Results of tension and Charpy impact tests are given in Table 3. In this table, "elastic limit" means the highest stress that leaves no appreciable permanent deformation after removal of the load; "proof stress" means the stress that results in a permanent deformation of 0.0001 in. per in. of length after removal of the load.

PART II—EFFECT OF CYCLIC STRESS RANGE ON CORROSION, AS ILLUSTRATED BY TYPE 2 GRAPHS

Effect of Stresses below Corrosion-fatigue Limit

The results of stage 2, or fatigue, tests may be expressed in the usual stress-cycle graphs. Such graphs on a semilogarithmic scale were presented in two previous papers.[6,7] From these graphs the fatigue limits of the previously corroded specimens were obtained. The estimation of fatigue limits from relatively few individual results is made easier by the fact that the stress-cycle graph for a corroded specimen, at least between abscissas corresponding to 1 and 10 million cycles, is nearly parallel to the ordinary endurance graph. The method of obtaining fatigue limits is illustrated in the two previous papers.

To save space in this paper the stress-cycle graphs have been omitted. The fatigue limits obtained from these graphs, however, are utilized in graphs of other types to illustrate the relationship between corrosion-stress, time, number of cycles, and the resultant fatigue limit.

TABLE 3.—*Results of Tension, Charpy and Endurance Tests*

Averages and Mean Departures from Averages

Material	Condition	Designation	Tensile Strength	Johnson's Limit	Proof Stress	Elastic Limit	Proportional Limit	Elongation in 2 In.	Reduction of Area	Charpy Impact Value, Ft.-lb.	Endurance Limit, Rotating Cantilever
			Lb. per Sq. In.					Per Cent.			Lb. per Sq. In.
Ingot iron	Annealed	IZ-17.5	42,600 ±300	15,000	15,000	10,800 ±300	10,500 ±500	47.0	69.0	10.4 ±0.9	24,000
0.24 per cent. carbon steel	Quenched and Drawn	IH-W-9	78,700[a] ±3,400	55,700[a] ±5,100	54,300[a] ±5,600	53,700[a] ±5,800	50,000[a] ±3,300	26.2[a] ±1.4	68.1[a] ±0.9	42.8[a] ±0.4	37,000
0.24 per cent. carbon steel	Annealed	IH-16.5	55,600[a] ±1,500	33,300[a] ±4,100	34,000[a] ±4,000	28,000[a]	24,700[a] ±1,100	39.0[a] ±1.3	59.7[a] ±1.8	12.1[a] ±2.2	24,000
Hign-carbon steel	Annealed	EM-14.75	103,400 ±4,100	60,300 ±2,800	60,600 ±2,900	55,800 ±3,700	49,500 ±2,300	29.5 ±1.3	50.8 ±2.4	12.9[a] ±1.3	42,000
Nickel steel	Quenched and Drawn	IW-W-9	140,200[b] ±3,600	125,900[b] ±4,300	127,800[b] ±4,200	123,500[b] ±4,800	112,500[b] ±5,000	18.1[b] ±1.0	59.9[b] ±0.7		
Nickel steel	Quenched and Drawn	IW-W-10	128,100[f] ±2,800	114,000[f] ±3,000	114,600[f] ±3,000	110,000[f] ±3,700	94,300[f] ±2,600	20.6[f] ±0.8	61.8[f] ±0.8	29.0	64,000
Nickel steel	Quenched and Drawn	IW-W-11	114,200[b] ±1,600	99,200[b] ±1,800	100,300[b] ±1,200	96,600[b] ±1,900	87,100[b] ±2,700	23.7[b] ±1.0	65.6[b] ±0.9		
Nickel steel	Annealed	IW-14.5	90,200[e] ±1,700	60,600[e] ±1,000	59,500[e] ±1,600	59,400[e] ±2,200	53,800[e] ±6,300	29.9[e] ±0.8	59.1[e] ±0.9		49,000
Silicon-nickel steel	Quenched and Drawn	HG-0-7.5	251,300[a] ±3,100	201,700[a] ±5,600	203,000[a] ±8,700	189,700[a] ±1,300	155,000[a] ±10,000	8.3[a] ±0.3	46.5[a] ±0.5	8.6 ±0.5	108,000
Chromium-nickel steel	Quenched and Drawn	BC-W-10	137,700[d] ±2,500	120,800[d] ±3,600	122,600[d] ±3,600	117,100[d] ±3,200	101,900[d] ±4,800	19.4[d] ±0.8	58.3[d] ±1.1	30.6 ±3.0	68,000
Chromium-nickel steel	Quenched and Drawn	AY-W-10	157,800[c] ±3,100	141,400[c] ±3,200	143,100[c] ±3,100	136,200[c] ±3,300	106,100[c] ±4,200	16.8[c] ±1.0	50.3[c] ±1.5		76,000

Unless otherwise indicated, each value is the average of two determinations, except endurance values.

a = Average of 3 determinations.
b = Average of 5 determinations.
c = Average of 7 determinations.
d = Average of 11 determinations.
e = Average of 19 determinations.
= Average of 23 determinations.

To represent by two-dimensional graphs the effect of corrosion-stress on resultant fatigue limit, the two other variables, time and number of cycles, must be held constant. Such graphs, called type 2 graphs, were presented in the two previous papers.

In Fig. 1 are shown type 2 graphs for carbon and alloy steels having a wide range of physical properties. Abscissas represent corrosion-stresses and ordinates represent resultant fatigue limits. Curves 1 and 2 in this figure represent results obtained by corrosion in fresh and salt water respectively. The corrosion time for each of these tests was 10 days, the cycle frequency 1450 r.p.m., and the total number of cycles about 20 million.

Type 2 graphs for some of these same materials were presented in a previous paper.[7] Since that time, however, additional results have been obtained which throw more light on some of the relationships.

Comparison of the ordinate of each of these graphs at its origin with the endurance limit of the metal, as listed in Table 3, shows that stressless corrosion for 10 days has lowered the fatigue limit considerably. The form of this type 2 graph, for carbon and ordinary alloy steels, has been described in the two previous papers. It was also pointed out in one of these papers[7] that the abscissas at which all these graphs first become nearly vertical differ only slightly for steels having a wide range of physical properties and chemical composition. The abscissa, about 7000 or 8000, at which the graph becomes nearly vertical was called a "notching stress" or "notching limit," because the dip in the type 2 graph corresponds to a change in the corrosion pits from the shallow pits of stressless corrosion to sharp, deep circumferential notches. It was also pointed out in that paper that the notching stresses for fresh and salt water are nearly the same.

The fact that the type 2 graph for ordinary steels, after its first steep descent, turns outward and becomes nearly horizontal before its final steep descent to the axis of abscissas, was discussed in the previous papers under the heading "Notch Depth Limitation." As a possible cause of this outward turning of the graph, it was suggested that with increase in notch depth the accumulation of corrosion products retards corrosion and thus opposes the effect of increasing stress. For this reason increase in corrosion-stress above the notching limit was assumed to have little effect on notch depth until, through stress concentration, the actual stress at the bottoms of the notches reached the endurance limit of the metal. The final descent of the graph to the axis of abscissas evidently corresponds to the second period of corrosion-fatigue described.

In the two previous papers it was suggested that the form of the nearly horizontal part of the type 2 graph might be influenced by another factor. As the notch depth increases during corrosion, and as the actual stress at the bottoms of the notches rises and approaches the endurance

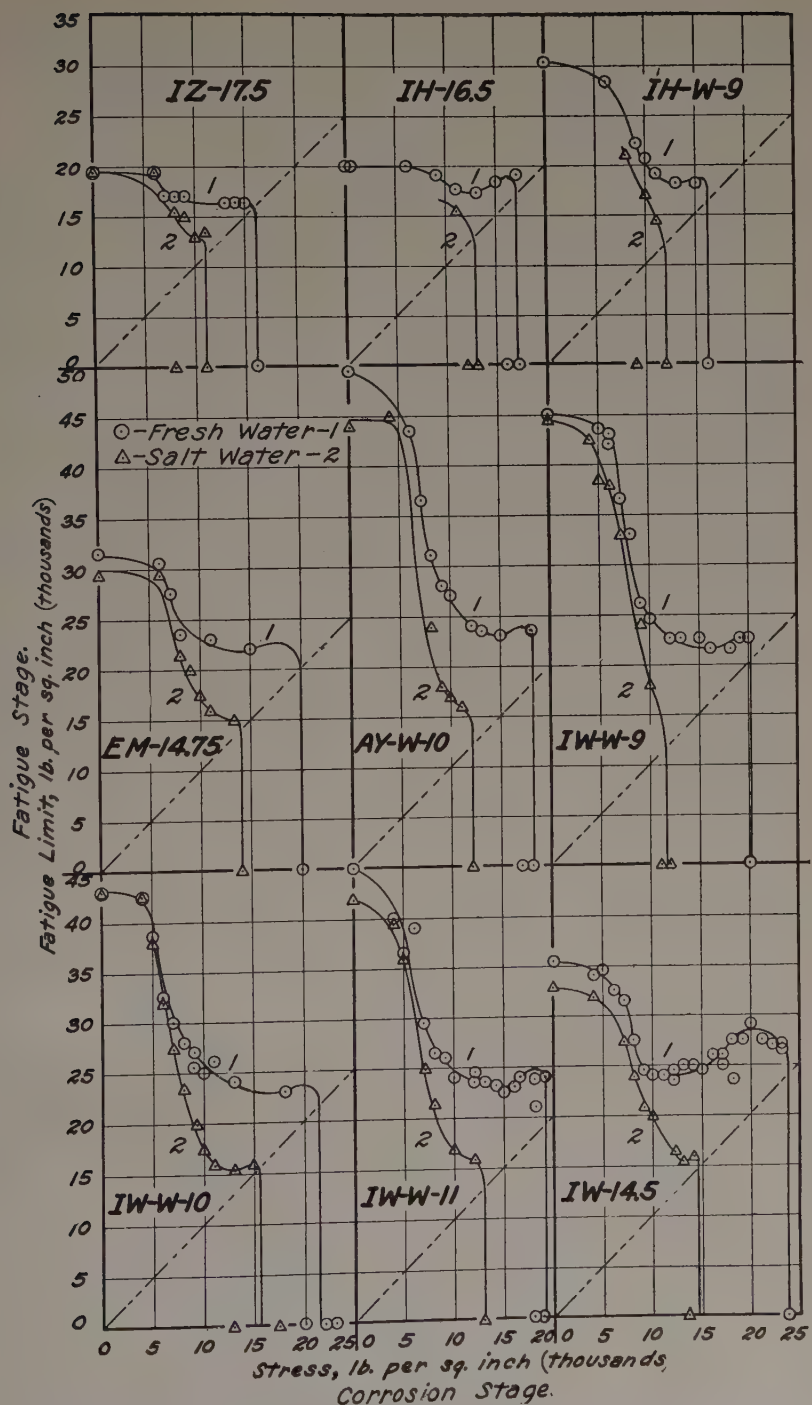

FIG. 1.—EFFECT OF CORROSION-STRESS ON FATIGUE LIMIT, TYPE 2 GRAPHS.

limit, it is possible that the endurance limit of the metal at the bottoms of the notches may be raised. In one of the previous papers[7] evidence was presented that for some steels the type 2 graph actually turns upward before its final descent to the axis of abscissas. This tended to confirm the suggestion that the form of the graph is influenced by the raising of the endurance limit at the bottoms of corrosion notches. It seemed desirable, however, to investigate this subject more fully and determine definitely whether, for some steels at least, the type 2 graph actually turns upward before its final descent. Additional evidence on this point, therefore, is presented in Fig. 1.

In the upper row of this figure are three sets of graphs, portions of which were presented in a previous paper.[7] As illustrated by the graph for material IH-16.5, and possibly for material IH-W-9, there is an indication that the fresh-water graphs turn upward just to the left of their final descent to the axis of abscissas. In the second row the fresh-water graph for material AY-W-10 gives the same indication.

To study further the form of the graph as affected by heat treatment, experiments were made with nickel steel that had been given four different heat treatments. The graphs obtained are those for materials IW-W-9, IW-W-10, IW-W-11, and IW-14.5. The first three were quenched and drawn at the indicated temperatures; the last named was fully annealed. The graphs are arranged in order of decreasing hardness of material. One of these graphs, that for material IW-W-10, was presented in a previous paper.[7]

It will be observed that the fresh-water graphs for materials IW-W-9, IW-W-11, and IW-14.5, and the salt-water graphs for materials IW-W-10 and IW-14.5, all show indication of an upturn just to the left of the final descent. The fresh-water graph for material IW-W-10 probably would show the same upturn if additional specimens were tested at suitable corrosion-stresses.

In the fresh-water graph for material IW-14.5, however, the upturn is prominent. The form of this graph is established by numerous individual tests. The rise begins at an abscissa corresponding to a stress of about 11,000, from which point the graph curves upward to an abscissa of about 20,000, then curves gradually downward until it begins a nearly vertical descent at an abscissa of about 24,000. As shown by this graph, corrosion-stress of 20,000 lb. per sq. in. lowers the resultant fatigue limit less than does corrosion-stress of 10,000 and no more than does corrosion-stress of 8000 lb. per square inch.

In view of the evidence presented, all the fresh-water graphs in Fig. 1 have been drawn with a slight rise above, and to the left of, the 45° line, though in some graphs enough individual points are not available to necessitate the drawing of an upturn in the graph. In view of the present evidence, all the fresh-water type 2 graphs in a previous paper[7] should probably have been drawn with the upturn.

The fact that the fatigue limit is elevated by the action of corrosion-stresses below the corrosion-fatigue limit tends to confirm the analysis of the corrosion-fatigue process given in several recent papers [4,6,7] and discussed briefly in Part I of the present paper. The conclusion seems to be well established that at the end of the first period of corrosion-fatigue the actual stress at the bottoms of the pits is at the endurance limit, though the nominal stress may be as low as the corrosion-fatigue limit.

That in ordinary fatigue tests the endurance limit of a metal can be elevated by cyclic stress not far below the original endurance limit is established by numerous scattered experiments reported by a number of investigators. As indicated in the fresh-water graph for material IW-14.5 in Fig. 1, the strengthening effect of cyclic stress is appreciable at corrosion-stresses less than half the corrosion-fatigue limit, and reaches a maximum at corrosion-stresses slightly below the corrosion-fatigue limit. This suggests the possibility that for ordinary fatigue tests in air the strengthening effect of understressing may be appreciable at stresses far below the original endurance limit. There is need for further investigation of this subject.

It is of interest to consider the position of each type 2 graph in Fig. 1 with reference to the diagonal broken line. In these graphs, the final reversal of curvature and the beginning of the steep descent to the axis of abscissas is above and to the left of the intersection of the graph with the diagonal line. In some of the graphs, such as the graph for materials AY-W-10, IW-W-11, IW-14.5, and in some of the graphs presented in previous papers[6,7] the final reversal of curvature is considerably above and to the left of the 45° line. According to the analysis mentioned, of the corrosion-fatigue process, the second period of the process begins when the actual stress at the bottoms of the notches reaches the endurance limit, and hence when the resultant fatigue limit has been reduced to equality with the corrosion-stress. Hence, if there were no strengthening of the metal at the bottoms of the notches, it would be expected that the final reversal of curvature would be exactly at the intersection with the 45° line. The fact that the final reversal is to the left of the intersection of the graph with the 45° line is probably due to the opposing influences of several factors.

These factors may be illustrated by reference to the graph for material IW-14.5 in Fig. 1. As indicated by this graph, with increase in corrosion stress from about 11,000 to 20,000, the resultant fatigue limit, and hence the endurance limit of the metal at the bottoms of the notches, is elevated. With this increase in the corrosion-stress, however, there is a slight increase in the depth and sharpness of notches, and hence some increase in stress concentration. The local hardening of the metal also tends to increase the stress concentration. As the corrosion-stress is increased the effect due to local elevation of the endurance limit at first

predominates. The increasing stress concentration due to increase in notch depth and to local increase in hardness, however, finally counterbalances the effect of increasing endurance limit. With further increase in corrosion-stress the effect of increasing stress concentration overbalances the effect of increasing endurance limit. It seems probable that the gradually descending portion of the graph for material IW-14.5 between abscissas of 20,000 and 24,000 is due largely to increasing stress concentration caused by hardening of the metal at the bottoms of the notches.

It was suggested in a previous paper[7] that there may be a third cause for the outward turning of the type 2 graph after its first steep descent. This third possible cause was not discussed in that paper. Results to be presented in the present paper indicate that the outward curvature of the type 2 graph represents a real relationship between corrosion-stress and resultant fatigue limit. The influence of accumulating corrosion products in retarding corrosion at the bottoms of the notches is now believed to be a relatively small factor in giving the complex form to the type 2 graph. This complexity of form is due chiefly to complexity of the actual relationship between the corrosion-stress and resultant fatigue limit. As explained above, however, this form is somewhat modified by the strengthening of the metal at the bottoms of the notches.

The relation between the salt-water and fresh-water graphs is more clearly indicated in Fig. 1 than in the previous paper.[7] As here shown, some of these salt-water graphs are entirely distinct in position from the fresh-water graphs. Though in the first steep descent the two graphs nearly coincide, they usually start at slightly different levels and the final reversal of curvature is at entirely different levels. The relation of the salt-water graphs to the diagonal broken line is similar to the relation of the fresh-water graphs to the same line.

Extension of Field of Investigation to Include Corrosion-stresses between Corrosion-fatigue Limit and Endurance Limit

In the investigation of corrosion by means of two-stage tests previously described the corrosion-stress has been below the corrosion-fatigue limit. As the corrosion-fatigue limit for carbon and ordinary alloy steels is low, while the endurance limit may be high, it seemed desirable to extend the field of investigation so as to include the effect of corrosion-stresses ranging from zero to the endurance limit. By thus extending the field, it was hoped that much more light would be thrown on the influence of stress, time, and number of cycles than had been possible while the investigation was confined to the relatively narrow range of corrosion-stresses between zero and the corrosion-fatigue limit. In using corrosion-stresses above the corrosion-fatigue limit, however, there is danger of carrying the corrosion stage so far that the first period of corrosion-fatigue

may be exceeded and the second stage entered. In this second stage, the actual stress at the bottoms of the notches would be above the endurance limit, and the progress of pitting would be due to fatigue as well as to corrosion. For purposes of this investigation, evidently, the second or fatigue period of corrosion fatigue must be avoided; the actual corrosion-stress must be kept below the endurance limit.

There is a definite criterion, however, which indicates whether or not the first period of corrosion-fatigue has been exceeded in the corrosion stage. If the resultant fatigue limit is not less than the corrosion-stress, the first period of corrosion-fatigue has not been exceeded. If the resultant fatigue limit is less than the corrosion-stress, the actual stress at the bottoms of the notches has exceeded the endurance limit. To avoid fatigue in the corrosion stage, therefore, the resultant fatigue limits must be kept above the 45° lines shown in Figs. 1 and 2. By keeping within the area above this 45° line, it has been found possible to extend the field of investigation to include corrosion-stresses between zero and the endurance limit.

In Fig. 2 are shown results of some tests in which the field of investigation of the type 2 graph has been thus widened. In some of the tests presented in this figure the corrosion-stresses were far above the corrosion-fatigue limit. In most of these two-stage tests, as shown by the position of the plotted points with reference to the 45° line, the first stage has been kept within the first or corrosion period of corrosion-fatigue. In some tests the corrosion stage has been carried beyond the first period of corrosion-fatigue. In the experiments represented in Fig. 2 and in all the following figures the corrosion medium was the previously described carbonate water.

The two series of graphs in Fig. 2 are type 2 graphs representing the effect of stage 1 tests at 1450 r.p.m. and 50 r.p.m., respectively, and for various corrosion times (and number of cycles). Each graph is designated by number indicating the corrosion time. The small circles representing experimental results are so designated only if they are not adjacent to corresponding graphs.

It was shown in a previous paper[7] that with increase in time and number of cycles in stage 1 the type 2 graph is moved downward and to the left. The results presented in Fig. 2 confirm the conclusion that the position and form of the type 2 graph vary with the time and number of cycles in the first stage.

The ordinates of the various graphs at the origin have been taken from a type 5 graph (yet to be described) made up of results of stressless corrosion tests for various times. The exact forms and positions of the various graphs have not been accurately determined, but they have been drawn with decreasing abruptness of reversal of curvature as the graph is moved upward and to the right. This is based on evidence to be presented later.

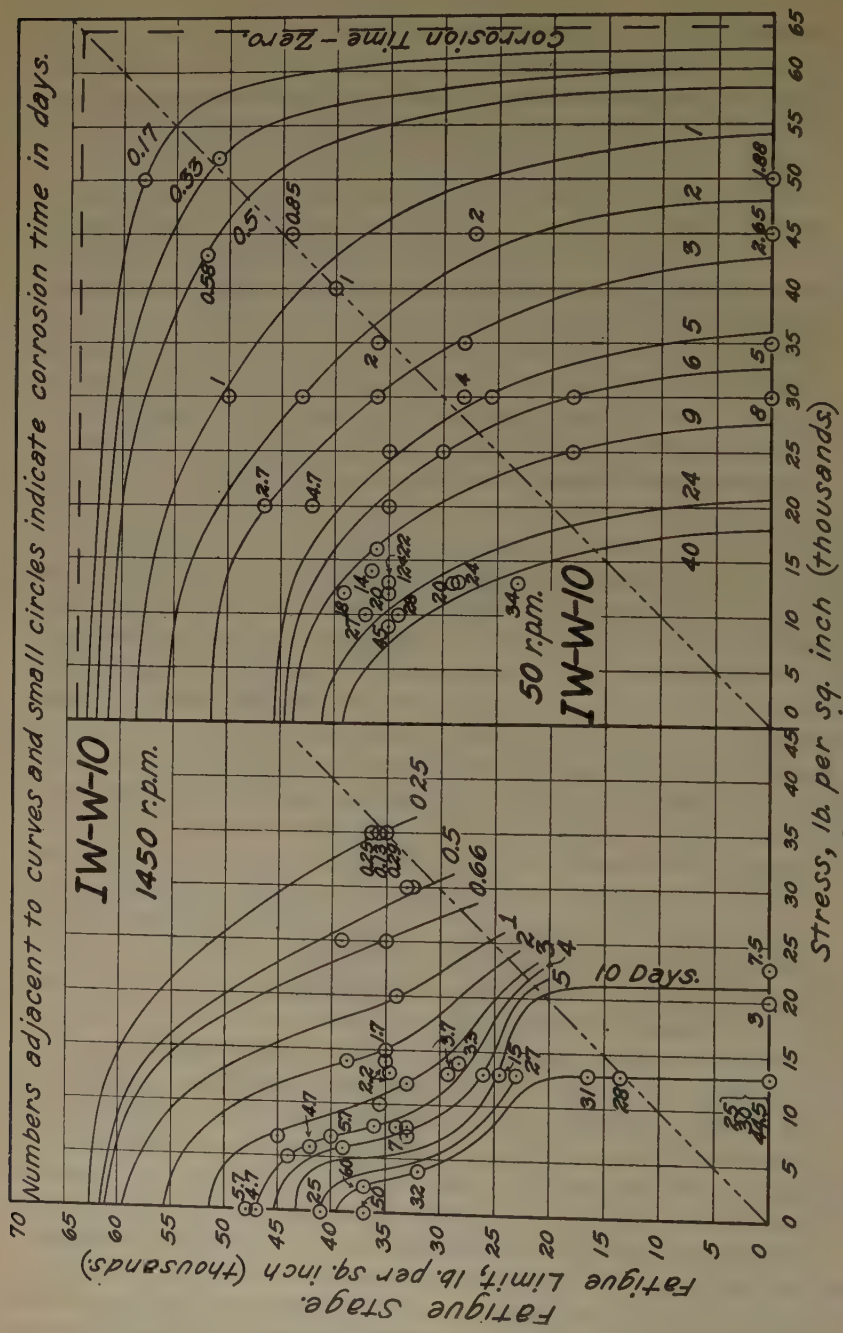

FIG. 2.—EFFECT OF VARYING CORROSION TIME AND NUMBER OF CYCLES ON THE FORM AND POSITION OF THE TYPE 2 GRAPH.

Instead of utilizing the type 2 graph further in this investigation, however, new types of graphs were developed, which proved more generally useful in representing the effect of stress, time and number of cycles on corrosion. Before describing these "constant-damage graphs," however, it is necessary to discuss in detail the type 5 graphs on which the constant-damage graphs are based.

Part III—Effect of Time and Number of Cycles on Corrosion, as Illustrated by Type 5 Graphs

Relation between Type 5 Graph and Type 4 Graph Presented in Previous Paper

In two previous papers[6,7] the effect of time and number of cycles on corrosion was illustrated by graphs called type 4, in which abscissas represented time and number of cycles, and ordinates represented "stress-concentration ratios." By "stress-concentration ratio" is meant the ratio of the endurance limit to the fatigue limit of the previously corroded specimen. For the purposes of the present paper, however, another type of graph has been found more useful. In this type, which has been called type 5, abscissas represent time (and number of cycles) in the corrosion stage and ordinates represent resultant fatigue limits. The type 5 is the most fundamental type of graph illustrating the relationship between stress, time, and number of cycles in causing penetration of metal under corrosion.

General Description of Type 5 Graph

In Figs. 3 to 8 are presented type 5 graphs illustrating the results of experiments at various corrosion-stresses and for various times and numbers of cycles. In these and the following figures the small circles representing experimental points are not designated by number unless they are not adjacent to the corresponding graphs. Each set of graphs represents results obtained at one cycle frequency. The uppermost (heavy line) graph in each series and the small solid circles in some series, represent results obtained by stressless corrosion. Each other graph represents results of corrosion under some one corrosion-stress. The ordinate of each graph at its origin represents the endurance limit of the metal and the course of each graph represents the decrease in the fatigue limit of the specimen with increase in the time and number of cycles in the corrosion stage.

Each individual point in these figures represents the result of a single two-stage test. From each of these tests the fatigue limit has been obtained by drawing a stress-cycle graph (not shown in this paper) parallel to the ordinary endurance graph, and taking as the fatigue limit

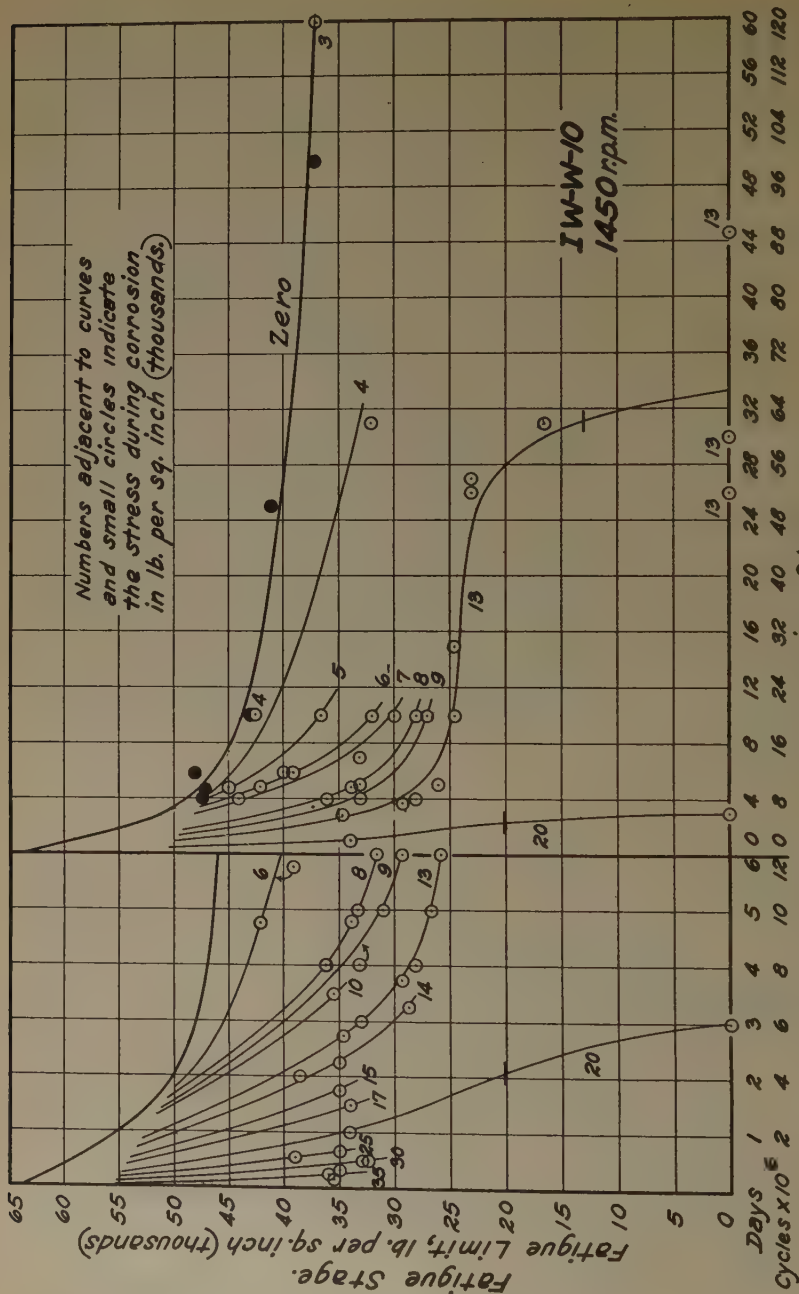

FIG. 3.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, NICKEL STEEL.

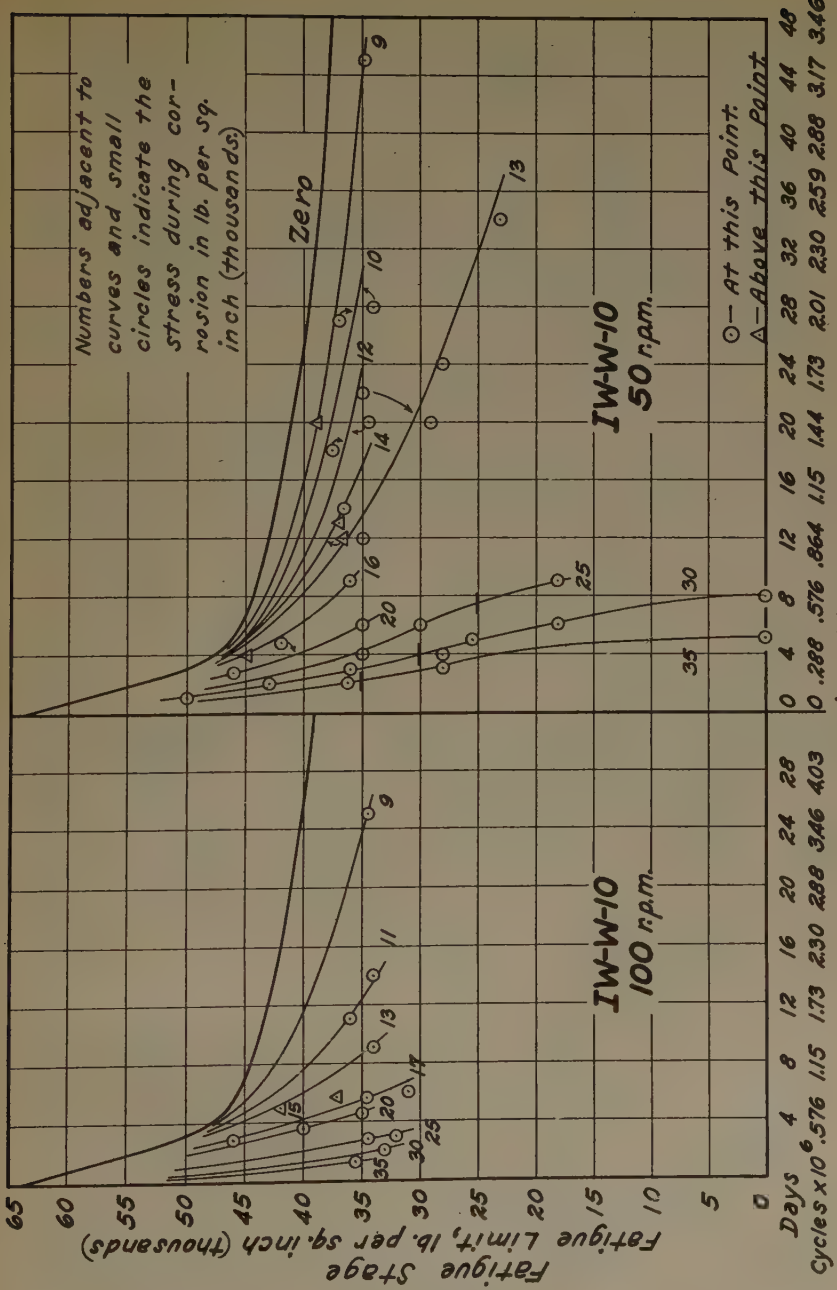

FIG. 4.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, NICKEL STEEL.

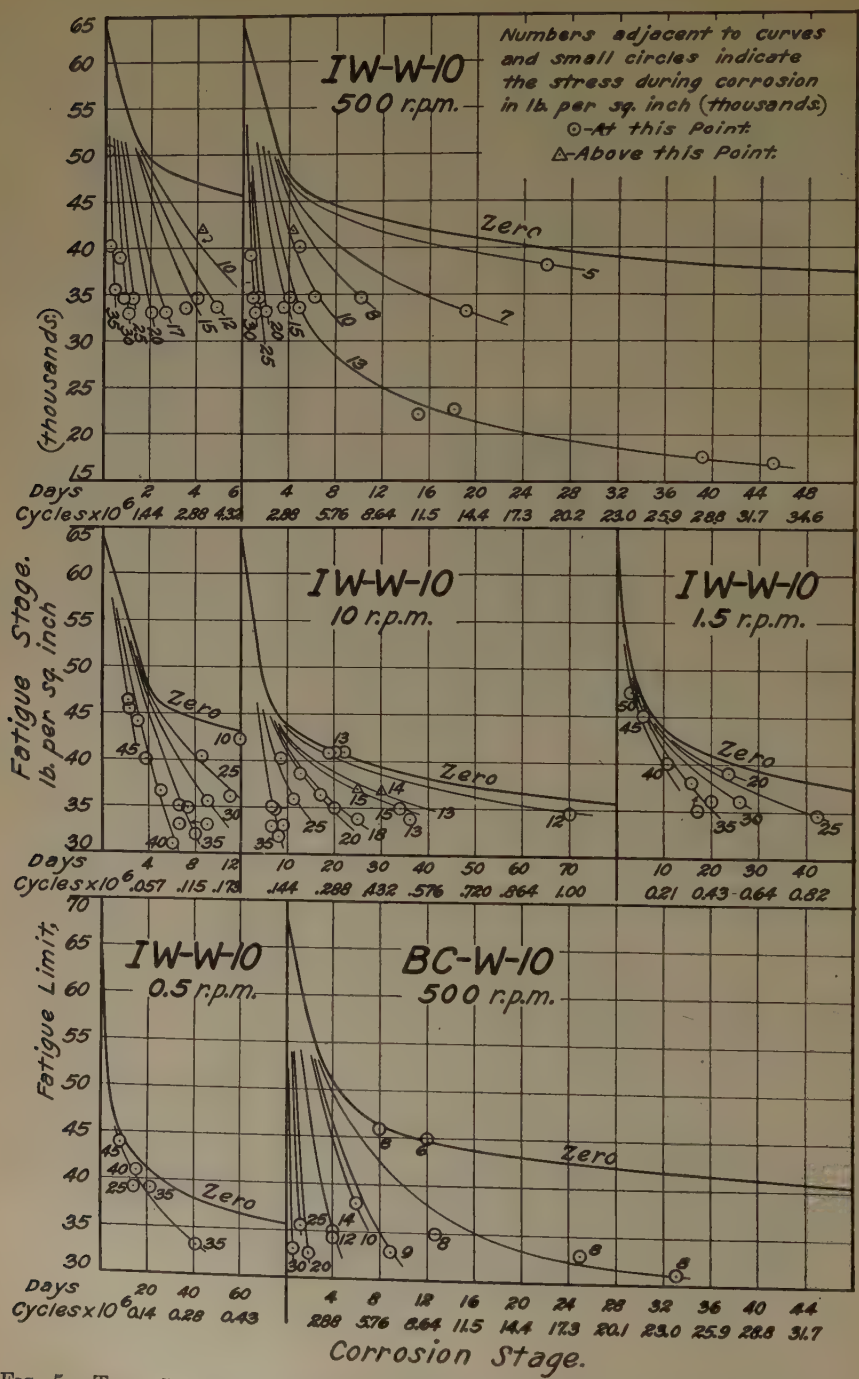

FIG. 5.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, NICKEL STEEL AND CHROMIUM-NICKEL STEEL.

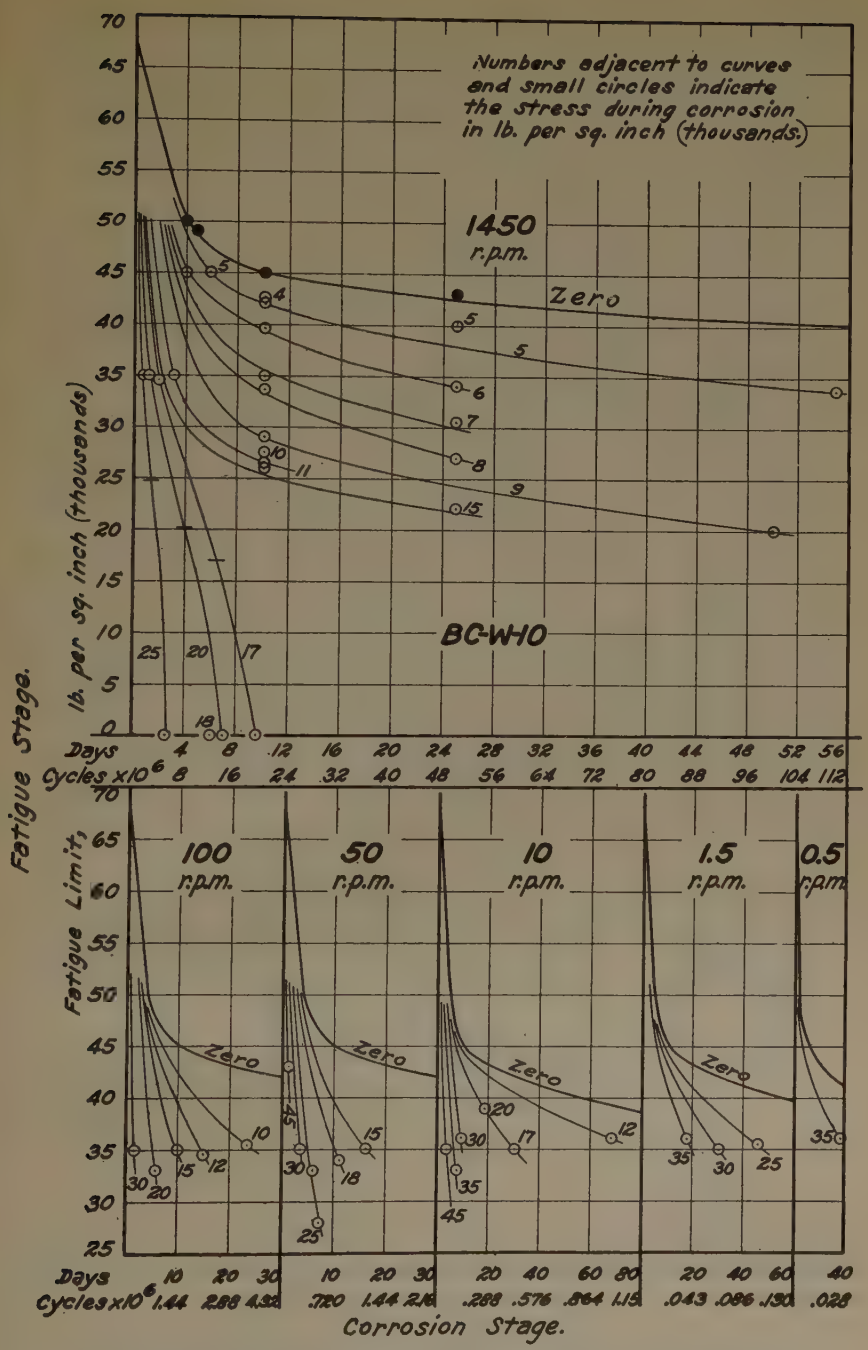

FIG. 6.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, CHROMIUM-NICKEL STEEL.

the ordinate of the graph at an abscissa of 10 million cycles. This method was illustrated in previous papers.[6,7]

Some of the graphs in Figs. 3 and 4 have been extended far enough to reach the axis of abscissas. By such graphs it is possible to follow the entire course of a corrosion-fatigue test at the indicated stress. The first period of the corrosion-fatigue test is represented by the course of the

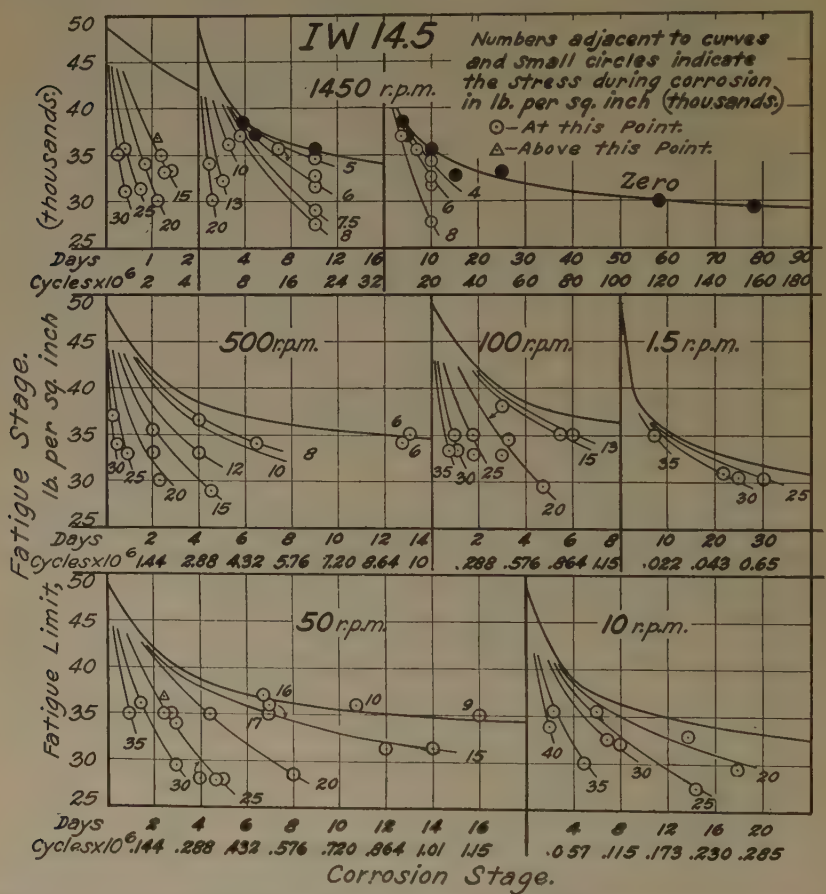

FIG. 7.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, ANNEALED NICKEL STEEL.

graph from its origin down to the point where the resultant fatigue limit of the specimen is equal to the corrosion stress. This point is indicated for various graphs in Figs. 3 to 8 by the short horizontal lines intersecting the graphs. At about this point in most of the complete type 5 graphs, there is evidently a reversal of curvature. This would be expected, as at this point the actual stress at the bottoms of the notches reaches the

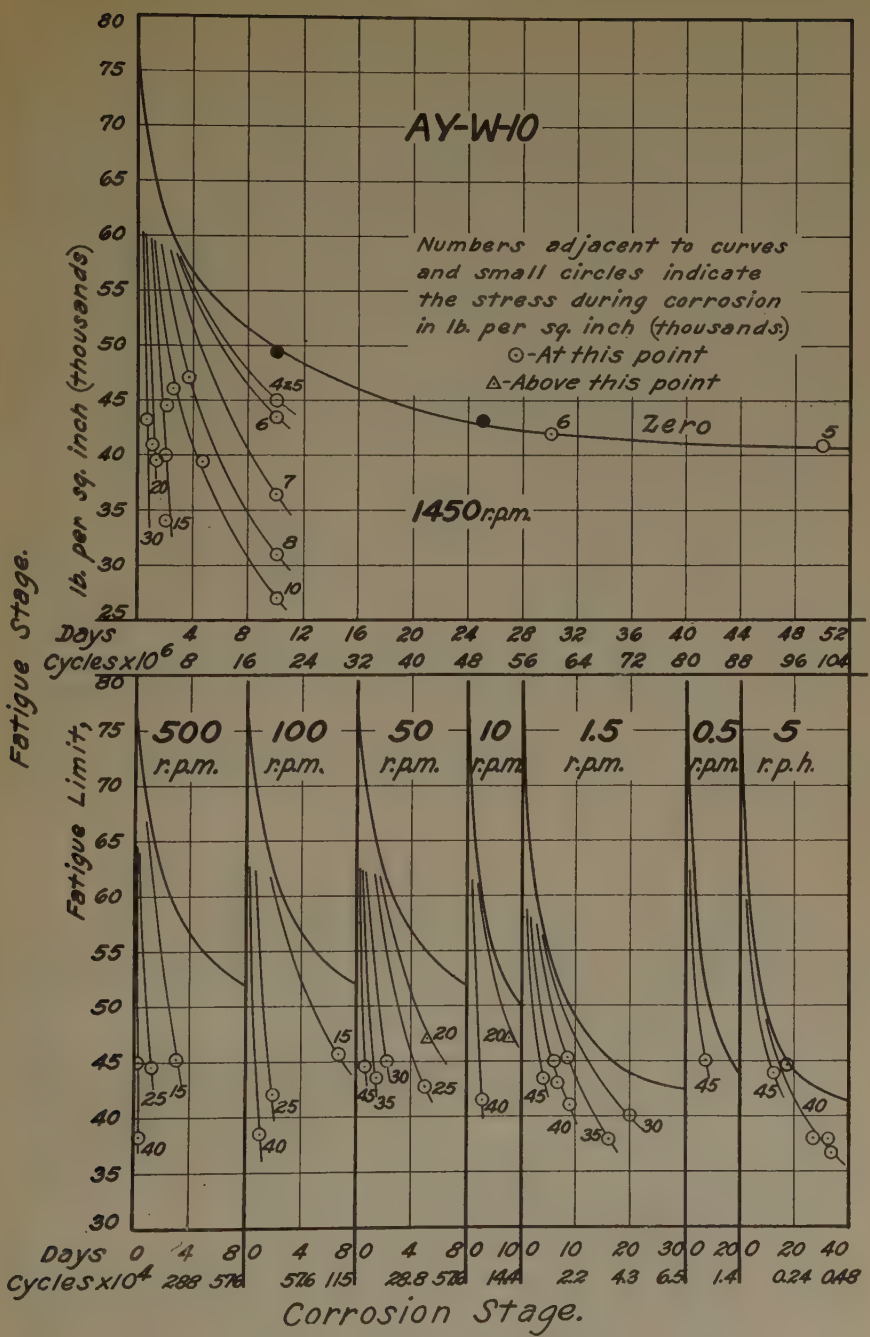

FIG. 8.—TYPE 5 GRAPHS, EACH REPRESENTING CONSTANT CORROSION-STRESS AND CONSTANT CYCLE FREQUENCY, CHROMIUM-NICKEL STEEL.

endurance limit of the metal and the cracks begin to advance at an accelerated rate.

If the corrosion-stress is below a more or less definite value, the type 5 graph, even if greatly prolonged, evidently would not reach the axis of abscissas. This is illustrated by the series in Fig. 3 and the series at the right of Fig. 4. The corrosion-stress below which the type 5 graph would not reach the axis of abscissas is the "corrosion-fatigue limit" for that material and cycle frequency. For purposes of this paper it was necessary to extend relatively few graphs to the axis of abscissas even when the corrosion-stress was above the corrosion-fatigue limit.

The point of reversal of curvature in some type 5 graphs is probably influenced by the elevation of the endurance limit at the bottoms of the notches. It is possible that this accounts for the indicated reversal of curvature of the 13,000 graph in Fig. 3 at a point well above the ordinate 13,000.

Derivation of Type 2 Graphs from Type 5 Graphs

Though the type 2 graphs presented in this and preceding papers were not obtained from type 5 graphs, they could have been so obtained. To obtain a type 2 graph from one of the sets of type 5 graphs in Figs. 3 to 8, the intersection of the type 5 graphs with a chosen vertical line may be used. The ordinates of these points become ordinates of the type 2 graph and the corresponding corrosion-stresses become the abscissas.

Derivation of Constant-damage Graphs from Type 5 Graphs

From any set of type 5 graphs, such as those shown in Figs. 3 to 8, it is possible to derive graphs of which each represents the corrosion-stress, time, and number of cycles necessary to reduce the fatigue limit to a chosen constant value. Such a graph may be called a constant-damage graph. From Fig. 3, for example, it is possible to derive a constant-damage graph representing the corrosion conditions necessary to reduce the fatigue limit to 35,000. To do this, the intersections of the type 5 graphs with the horizontal line representing a resultant fatigue limit of 35,000 would be used. In the same way, other constant-damage graphs could be obtained from Fig. 3 and from Figs. 4 to 8.

Constant-damage graphs of several types are discussed in Parts IV and V. In obtaining these graphs, the type 5 graphs were plotted on scales that were most suitable for the purpose. The type 5 graphs presented in Figs. 3 to 8 are merely illustrative and are not necessarily on the same scales that were used in obtaining the constant-damage graphs described in Parts IV and V.

Part IV—Constant-damage Graphs and Surfaces—Cartesian Coordinates

Advantages of Constant-damage Graphs

One disadvantage of variable-damage graphs, such as the type 2 and type 5 graphs discussed in Parts II and III and in the two preceding papers,[6,7] is that the relationship between corrosion-stresses represented by such graphs is merely the relationship between initial corrosion-stresses. The actual corrosion-stress, owing to increasing stress-concentration, increases throughout the corrosion stage; the increase becomes greater as the depth of pitting increases (as the resultant fatigue limit decreases). Moreover, the form of a variable-damage graph may be affected by varying accumulation of corrosion products in pits of varying depth. A variable-damage graph, therefore, is not a correct proportionate representation of actual average corrosion-stresses. It seemed possible, therefore, that the complexity of form of the type 2 variable-damage graph might be due in part to the fact that the graph represents merely initial rather than actual average corrosion-stresses. In such graphs, the influence of a stress-concentration variable is present but hidden.

In constant-damage graphs, however, the stress-concentration factor and the effect of corrosion products are minimized. For such graphs the resultant fatigue limit is a constant; hence the stress-concentration ratio is a constant. The depth of pitting is much more nearly constant than in a variable-damage graph. Actual relationship of corrosion-stresses is more correctly represented by constant-damage than by variable-damage graphs.

Type 6 Graph

Constant-damage graphs are presented in Figs. 9 to 14. All these graphs were obtained with the same nickel steel, material IW-W-10. To obtain a constant-damage graph, the resultant fatigue limit is held constant. By holding one other factor, or the ratio between two other factors, constant several types of constant-damage graphs can be obtained. By holding the cycle frequency in the corrosion stage constant, the type 6 graph is obtained.

In Fig. 9 are shown a series of type 6 graphs obtained from the set of type 5 graphs for nickel steel, IW-W-10, shown at the right of Fig. 4. Each graph in Fig. 9 is obtained from the points of intersection of the type 5 graphs of Fig. 4 with a chosen line of constant ordinates (resultant fatigue limits).

In following the course of each of the graphs in Fig. 9, it is most convenient to start at the end representing highest corrosion-stress. Each graph starts at the corrosion-stress that equals the resultant fatigue limit. The graph can not extend to the right of this point, as at higher

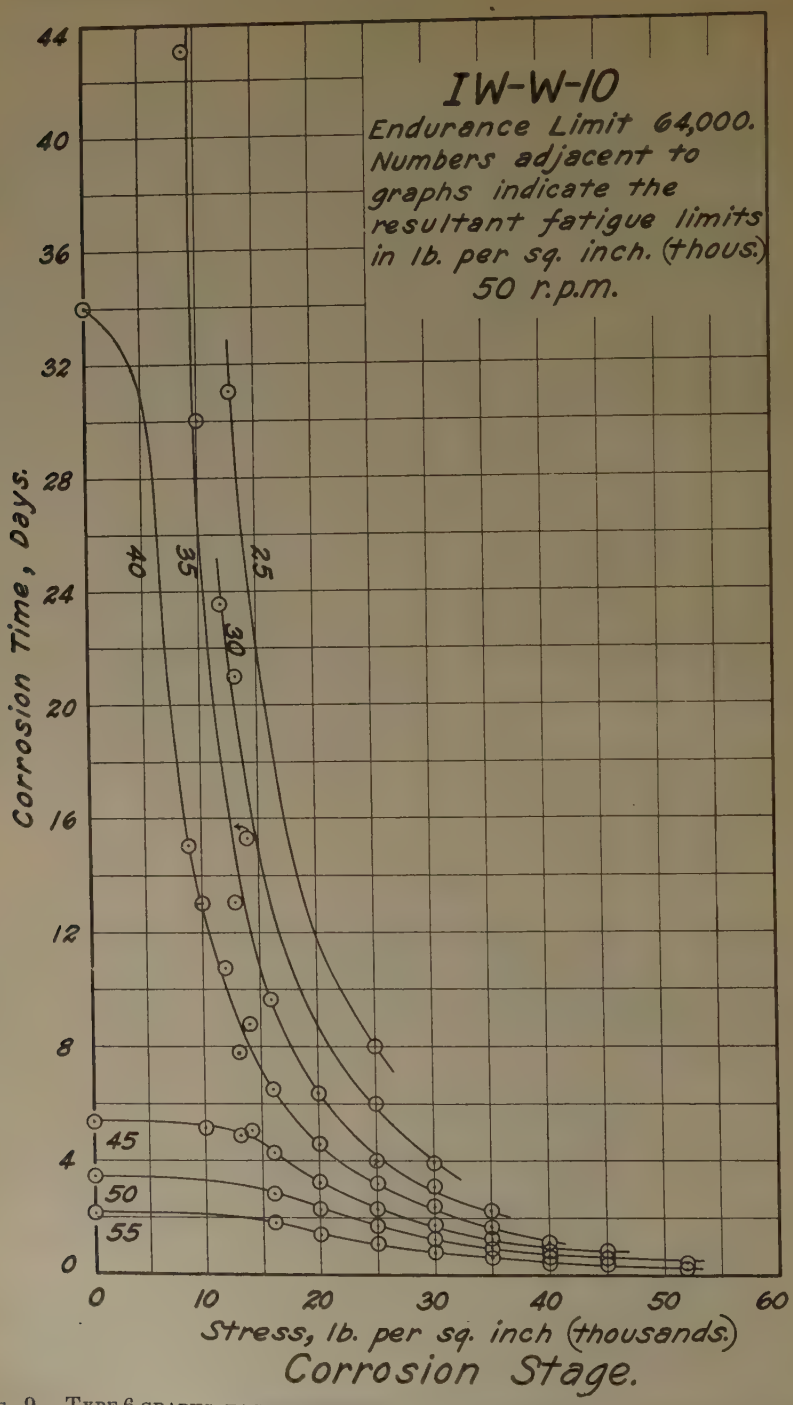

FIG. 9.—TYPE 6 GRAPHS, EACH REPRESENTING CONSTANT FATIGUE LIMIT AND CONSTANT CYCLE FREQUENCY, NICKEL STEEL.

corrosion-stresses the first period of corrosion-fatigue would be exceeded before the fatigue limit had been reduced to the desired value. With decrease in the abscissas the graphs in Fig. 9 all curve upward. Each of the lower four graphs then turns abruptly to the left and extends in a nearly horizontal direction to the axis of ordinates. These four graphs of complex form are obtained from constant-ordinate lines in Fig. 4 that intersect the stressless-corrosion line. When the chosen fatigue limit is so low that the constant ordinate line in a type 5 series does not intersect or approach closely the stressless-corrosion line, the type 6 graph is of simple form. There is no reversal of curvature of the type 6 graph unless it is extended so far that stressless corrosion alone for the indicated time would reduce the fatigue limit to the chosen value. If extended far enough, all the graphs in Fig. 9 would encounter a reversal of curvature and intersect the axis of ordinates. The type 6 graph, therefore, is of simple form except where it is distorted by relatively large effect of stressless corrosion. The simple type 6 graph on a scale of Cartesian coordinates appears to be approaching an asymptote nearly parallel to the time-cycle axis.

The complex type 6 graphs are somewhat similar in form to the type 2 graphs. With increase in corrosion-stress from zero, each type of graph first approaches the axis of abscissas at an increasing rate; the curvature then reverses and the graph tends to become parallel to the axis of abscissas. This similarity in form of the two types might have been expected, as the type 2 graph represents constant corrosion time and variable fatigue limit, whereas the type 6 graph represents variable corrosion time and constant fatigue limit. In both types, the other independent variable is corrosion-stress. The point of reversal of curvature in the type 6 graph, therefore, corresponds to the "notching limit" or "notching stress" discussed in two previous papers.[6,7]

The outward curvature of the type 2 graph between the two steep descents toward the axis of abscissas is evidently a qualitatively correct representation of the influence of cyclic stress range on corrosion. With increase in corrosion-stress beyond the notching stress, the effect of the corrosion-stress increases at a decreasing rate. It has been shown in previous papers,[6,7] that with increase in corrosion time and number of cycles the resultant fatigue limit is lowered at a decreasing rate. The same fact is shown by the type 5 graphs in Figs. 3 to 8. In this respect, therefore, the three variables, corrosion-stress, time, and number of cycles are qualitatively similar.

Effect of Cycle Frequency on Form and Position of Type 6 *Graph*

The two series of graphs in Figs. 10 and 11 have been arranged to show the effect of cycle frequency on the form and position of the type 6 graph. The graphs in these two figures have been obtained from the

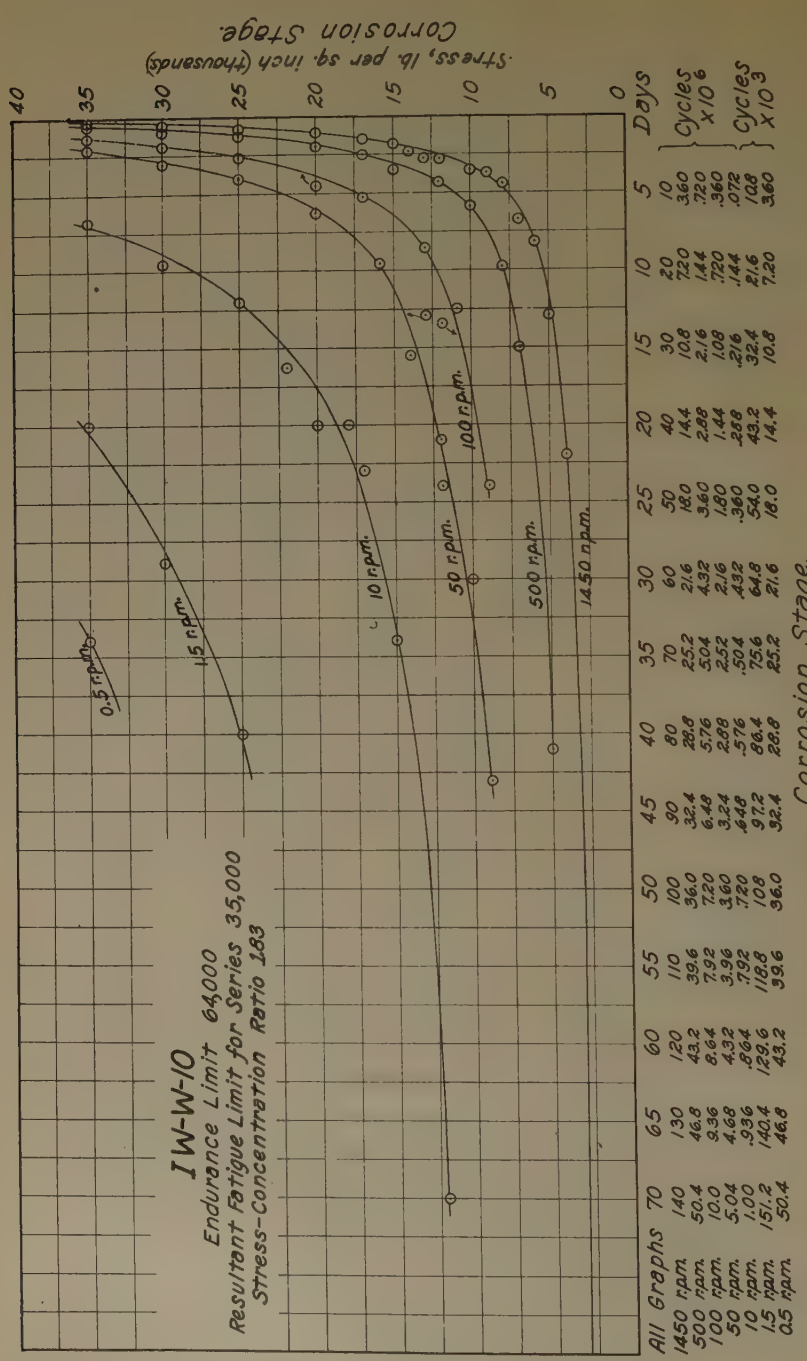

FIG. 10.—TYPE 6a CONSTANT-DAMAGE SERIES, NICKEL STEEL.

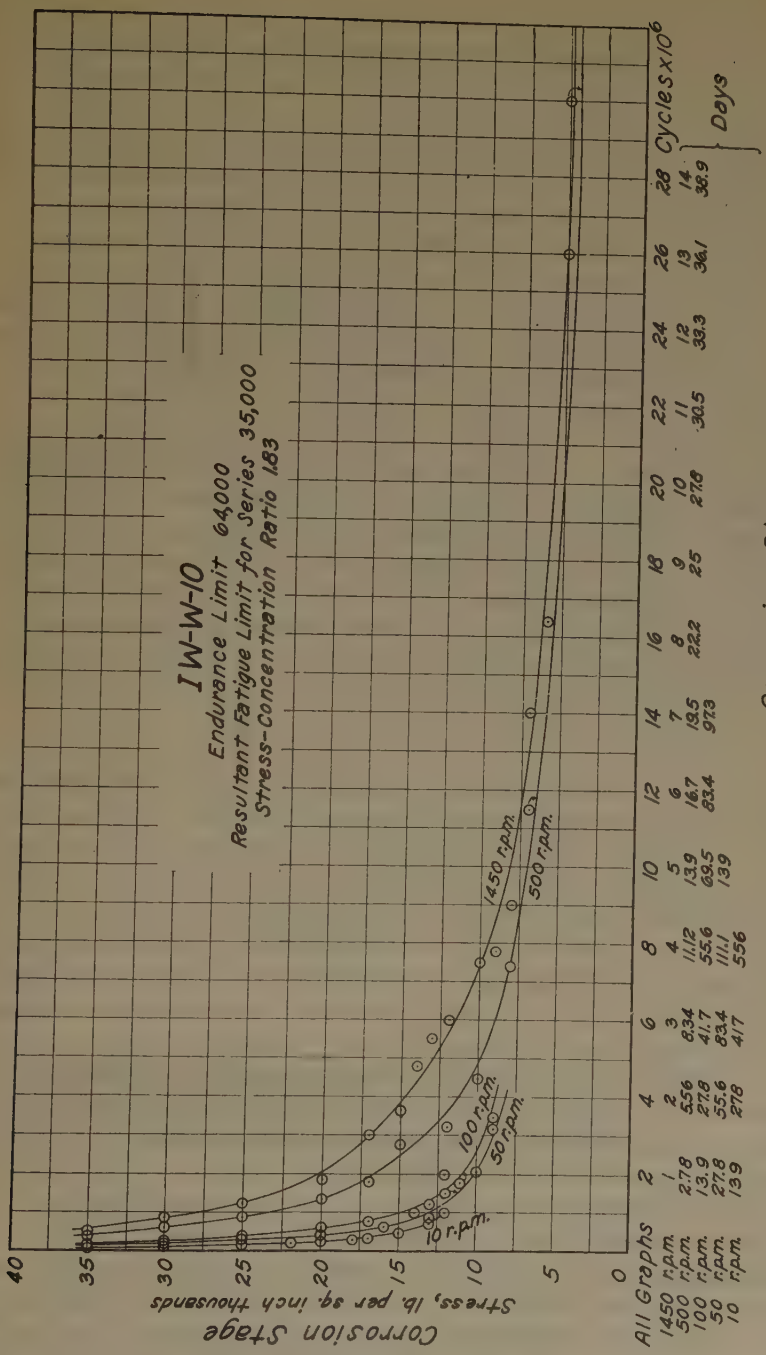

Fig. 11.—Type 6b constant-damage series, nickel steel.

type 5 graphs for material IW-W-10 in Figs. 3, 4, and 5. In Figs. 10 and 11, not only is each graph a constant-damage graph, but each series is a constant-damage series. In Fig. 10, all the graphs are arranged on the same time scale, but each graph has its own cycle scale. In Fig. 11, all the graphs are arranged on the same cycle scale, but each graph has its own time scale. The former will be called a type 6*a* series; the latter, a type 6*b* series.

In the type 6*b* series as represented in Fig. 11 the direction of abscissas is the reverse of the direction of abscissas in Fig. 10. This reverse arrangement in the two figures is to permit imaginary assembling of Figs. 10, 11 and 14 in three planes, each perpendicular to the other two, so as to represent projections (on the three planes) of lines on a constant-damage surface. Constant-damage surfaces will be discussed later.

In the type 6*a* series, as shown in Fig. 10, the position of the graph is lowered as the cycle frequency increases. This means that the time rate of penetration increases with increase in the cycle frequency. In the type 6*b* series shown in Fig. 11, the position of the graph is lowered as the cycle frequency decreases. This means that the penetration per cycle increases with increase in time per cycle (decrease in cycle frequency). These two figures will be discussed later as representing two side views of lines on a constant-damage surface.

Type 7 *and Type* 8 *Graphs*

As the type 6 graph represents constant-damage and constant-cycle frequency, one of the coordinates represents both time and number of cycles. It seemed desirable, therefore, to develop constant-damage graphs to represent the relationship between corrosion-stress and either time or number of cycles alone. Such graphs can be obtained from either the 6*a* or 6*b* series shown in Figs. 10 and 11. If the intersections of the series in Fig. 11 with one of the ordinate scale lines are so used, a graph will be obtained to represent relationship between corrosion-stress and time, for constant damage and constant number of cycles. This type, which has been called type 7, is shown in Fig. 12. Similarly, type 8 graphs can be derived from the 6*a* series in Fig. 10 to represent the relationship between corrosion-stress and number of cycles, for constant damage and constant time. A series of such graphs derived from Fig. 10 is shown in Fig. 13.

A comparison of Figs. 9 to 13 shows that the type 7 and type 8 graphs are similar in form to the type 6 graph. Undoubtedly if the type 7 (but not the type 8) graphs were prolonged far enough the influence of stressless corrosion would become relatively large enough to affect the form of these graphs as it affects the form of the type 6 graph, causing reversal of curvature. The steepness of the type 8 graph near the origin

shows the great influence of even a few cycles of high corrosion-stress in causing penetration of metal under corrosion.

The Type 9 Graph

In the same manner that the type 6 graph is obtained, it is possible to develop from a series of type 5 graphs another type of constant-damage

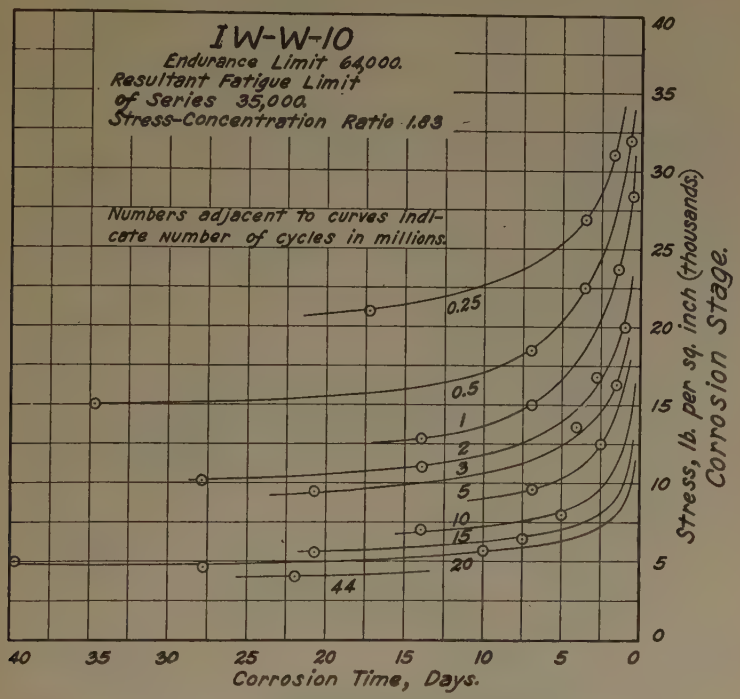

FIG. 12.—TYPE 7 CONSTANT-DAMAGE SERIES, NICKEL STEEL.

graph to represent the relationship between time and number of cycles, with constant corrosion-stress and constant resultant fatigue limit. A series of these type 9 graphs is shown in Fig. 14. Not only is each graph in Fig. 14 a constant-damage graph, but the entire series is a constant-damage series.

It will be observed that the type 9 graph is similar in form to the types 6, 7, and 8 graphs. Drawn with Cartesian coordinates, the type 9 graph appears to approach at each end an asymptote nearly parallel to the coordinate axis. If sufficiently prolonged, as indicated qualitatively in Fig. 14, this graph is influenced by the effects of stressless corrosion. Its curvature is reversed and it approaches the axis of abscissas at a point which represents the time required for stressless corrosion to cause

the same amount of damage. The broken line drawn through this point parallel to the axis of ordinates will be called the "time boundary" of the series. As shown in Fig. 9, there is a similar time boundary for each type 6 series.

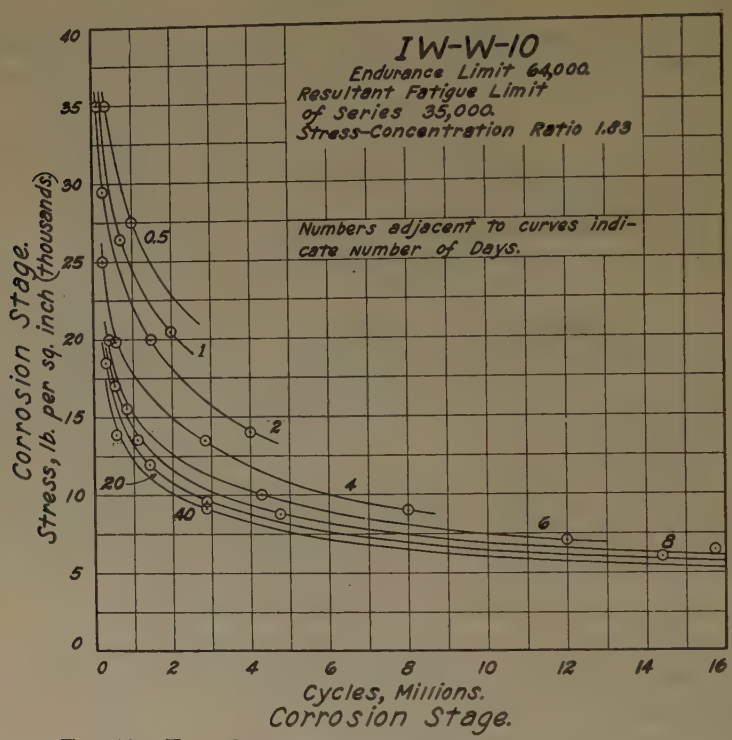

FIG. 13.—TYPE 8 CONSTANT-DAMAGE SERIES, NICKEL STEEL.

Constant-damage Surfaces

This type 9 series may best be studied by imagining it to be the plan view of a three-dimensional representation of the effect of stress, time and number of cycles on corrosion.

If an axis of corrosion-stresses be imagined perpendicular to the plane of Fig. 14 at the origin of coordinates, the type 9 graphs in this figure would be viewed as contour lines on a constant-damage surface. This constant-damage surface evidently slopes downward as it recedes from the imagined vertical axis of corrosion-stresses. With decrease in the corrosion stress, as indicated by the increasing distance between adjacent contour lines, the slope decreases. With decrease in the corrosion-stress below about 8000 lb. per sq. in. the constant-damage surface (on the scale represented in Fig. 14) evidently becomes nearly horizontal.

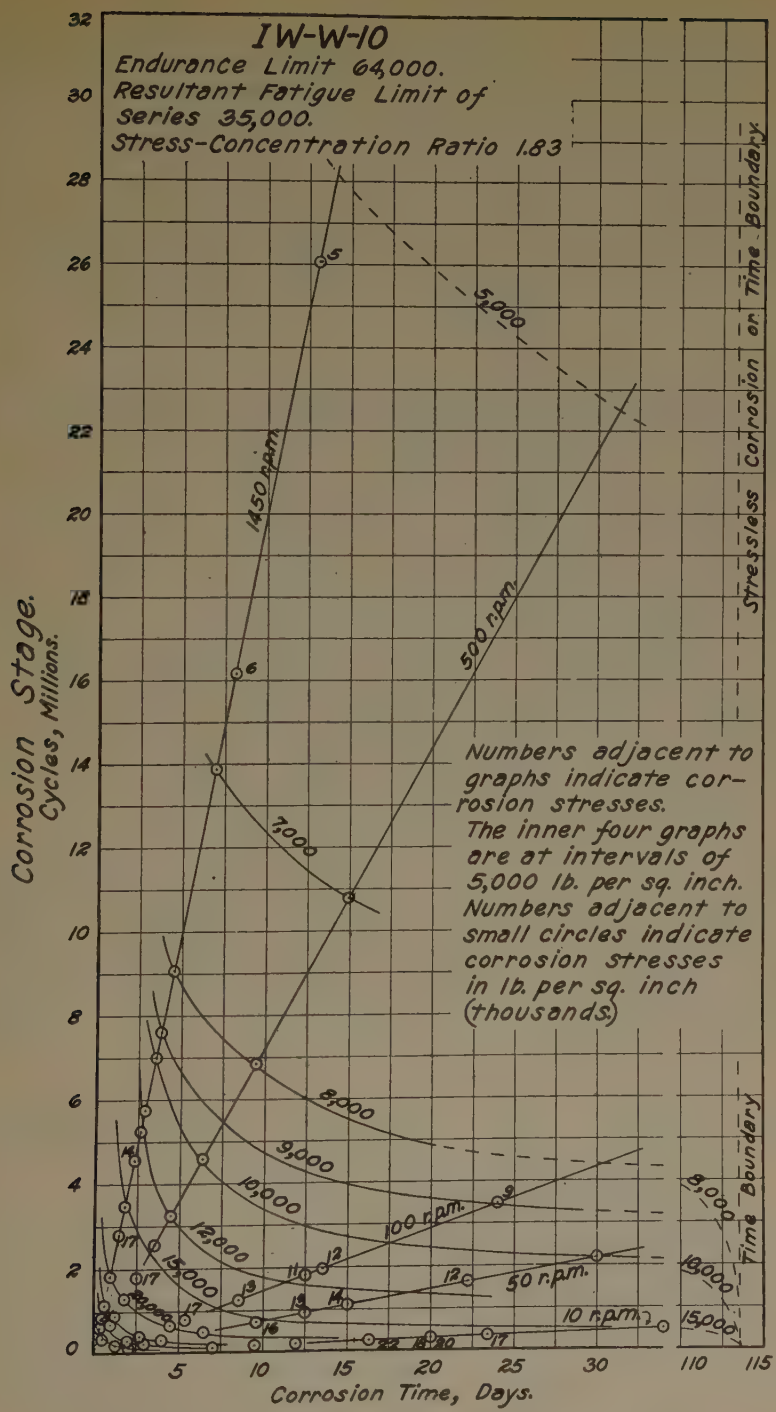

FIG. 14.—TYPE 9 CONSTANT-DAMAGE SERIES, NICKEL STEEL.

If Fig. 14 is considered as the plan view of contour lines in a constant-damage surface, Figs. 10 and 11 can be considered as front and side views of constant-frequency lines in the same surface. As shown in Fig. 14, these constant-frequency lines radiate from the imagined vertical axis of corrosion-stresses. If Figs. 10, 11 and 14 be imagined as properly assembled so that each is perpendicular to the other two, the type 6*a* series of graphs in Fig. 10 would represent a view of the constant-frequency lines from the distant end of Fig. 14 (in a direction parallel to the axis of cycles). The type 6*b* series in Fig. 11 would represent a view of the same lines from the right of Fig. 14 (in a direction parallel to the time axis).

If Figs. 12, 13 and 14 be imagined as properly assembled so that each plane is perpendicular to the other two, the types 7 and 8 graphs in Figs. 11 and 12 would represent two views of lines that are parallel to the planes of Figs. 12 and 13, respectively.

The constant-damage surface, as shown in Fig. 14, is concave upward, except in the region adjacent to the time boundary of the series. As indicated by the prolongation of some of the contour lines at the right of Fig. 14, the lines in this region reverse their curvature and approach a vertical plane through the axis of abscissas. The broken line marked "time boundary," toward which all the type 9 graphs of the series converge, may be viewed as a projection of a vertical plane which is the boundary of the constant-damage surface. The position of this time-boundary plane has been determined approximately by extrapolation of the type 5 stressless corrosion graph shown in Fig. 3.

There is some advantage in considering the vertical time-boundary plane as the origin of the series of contour lines (type 9 graphs) in Fig. 14. The course of each type 9 graph as it extends to the left of the time boundary then represents the decrease in corrosion time with increase in number of cycles. The entire constant-damage surface represents the effect of corrosion-stress and number of cycles in decreasing the corrosion time below the time necessary to cause the same amount of damage by stressless corrosion alone.

Part V—Constant-damage Graph and Surfaces, Logarithmic Coordinates

Types 9 Graphs, Logarithmic Coordinates

The type 9 graph on a logarithmic scale is the most generally useful type that has yet been developed. On a Cartesian scale the curvature of the type 9 graph is so great that interpolation and extrapolation are difficult. Moreover, as shown in Fig. 14, the range of cycle frequencies that can be represented in one constant-damage series is much less than is desirable. On a logarithmic scale, however, as shown in Fig. 15, the

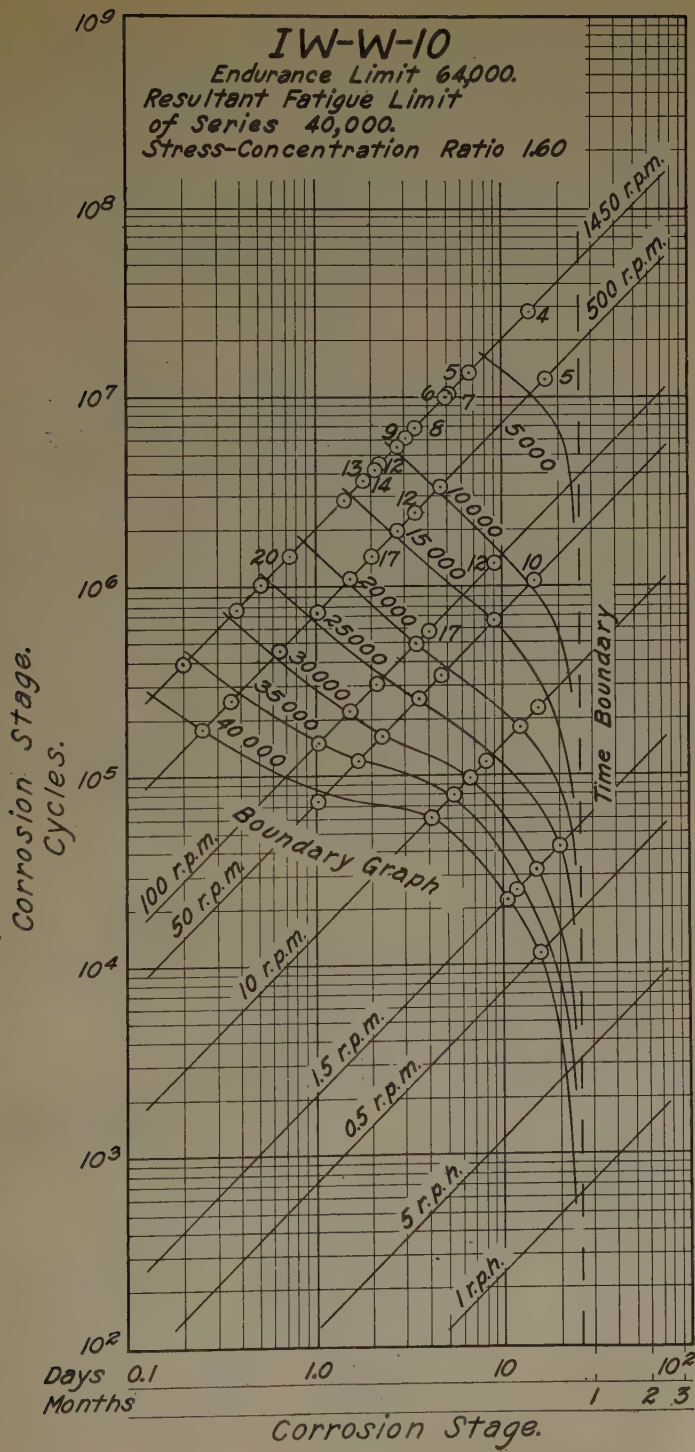
IW-W-10
Endurance Limit 64,000.
Resultant Fatigue Limit
of Series 40,000.
Stress-Concentration Ratio 1.60
1450 r.p.m.
500 r.p.m.
5000
10000
15000
20000
25000
30000
35000
40000
Time Boundary
Boundary Graph
100 r.p.m.
50 r.p.m.
10 r.p.m.
1.5 r.p.m.
0.5 r.p.m.
5 r.p.h.
1 r.p.h.
Corrosion Stage.
Cycles.
Days 0.1 1.0 10 10²
Months 1 2 3
Corrosion Stage.

Fig. 15a.

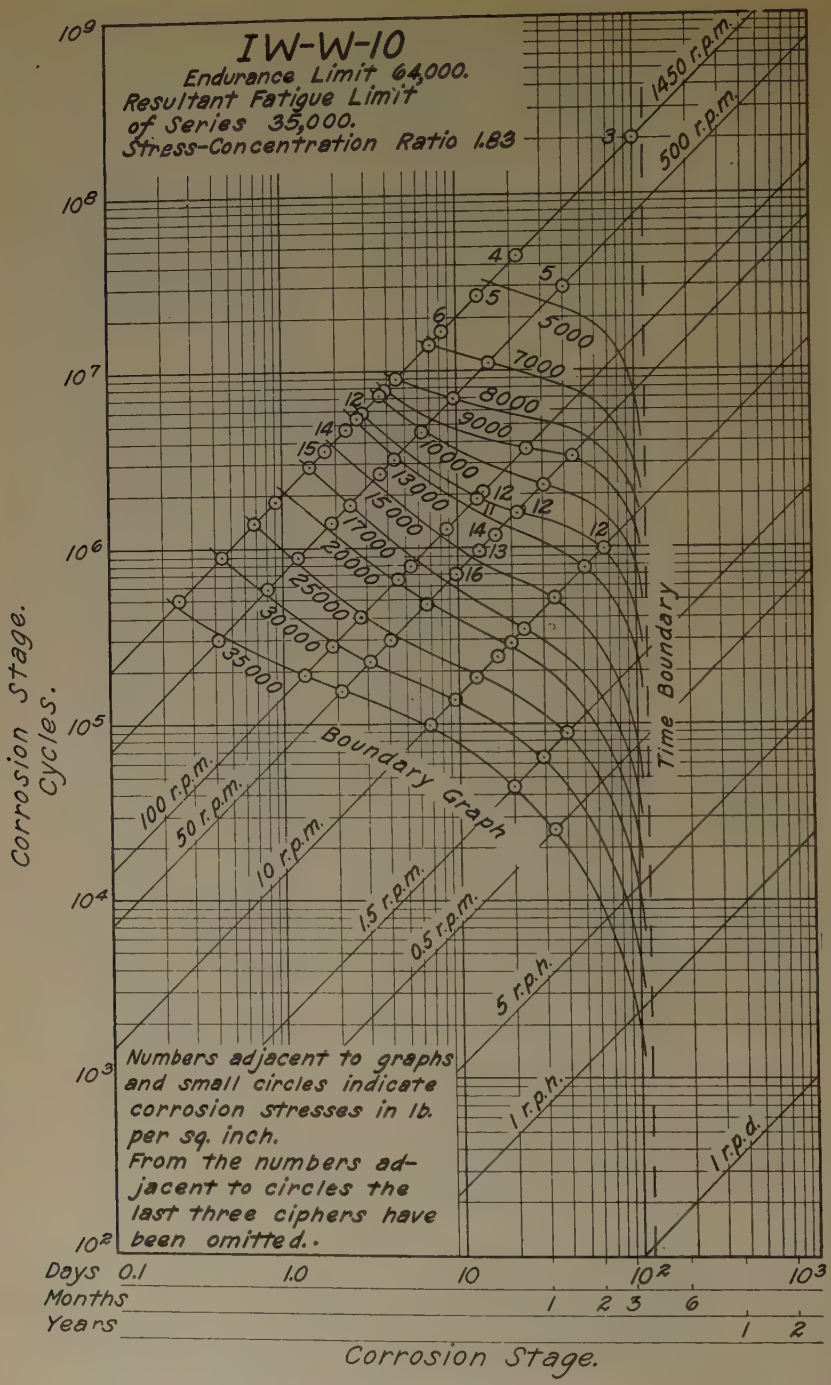

Fig. 15b.

Fig. 15.—Type 9 constant-damage series, nickel steel.

curvature is greatly reduced. The lines of constant frequency, which on a Cartesian scale are radiating lines, on a logarithmic scale become parallel diagonal lines. It is thus possible to include in one constant-damage series a wide range of corrosion-stresses and cycle frequencies. In Fig. 15 the range of actual cycle frequencies is from 1450 to 0.5 per minute. Additional constant-frequency lines, moreover, have been added wherever possible to represent 5 cycles per hour, 1 cycle per hour, and 1 cycle per day. These are designated 5 r.p.h., 1 r.p.h., and 1 r.p.d. respectively.

Type 9, *Constant-damage Series, Material IW-W*-10

Two series of type 9 graphs are shown on a logarithmic scale in Fig. 15. The two series in Figs. 15*a* and 15*b* represent corrosion conditions necessary to reduce the fatigue limit to 40,000 and 35,000, respectively. The series shown in Fig. 15*b*, therefore, represents greater stress-concentration ratio, and hence greater depth of pitting, than does the series shown in Fig. 15*a*.

In drawing the graphs of these series, and other series to be described, consideration has been given to each series as a whole. Each graph has not been based merely on its own experimental points, but has been drawn to represent the most probable relationship to neighboring graphs.

The "boundary graph" of each of these series is a graph obtained with corrosion-stress equal to the resultant fatigue limit. Higher corrosion-stresses could not be used, otherwise the first period of corrosion-fatigue would be exceeded before the resultant fatigue limit was reduced to the desired value. The other boundary of each series is the broken line designated "time boundary." This line has the same significance as in Fig. 14. It represents the time necessary to reduce the fatigue limit to the chosen value by stressless corrosion alone. The position of the time boundary for Fig. 15*b* has been determined as yet only approximately by extrapolation. For Fig. 15*a* the position of the time boundary has been determined definitely.

The curvature of the type 9 graph on a logarithmic scale is qualitatively similar to the curvature of this graph on a Cartesian scale. The curvature is slight, however, unless the graph is extended so far to the right that it approaches the time boundary of the series. All the graphs of a series, as they approach the time boundary, reverse their curvature, converge toward the time boundary, and approach the axis of abscissas.

All the graphs of a series, except possibly some of the low-stress graphs, are not far from parallel, unless they are extended so far to the right that they approach the time boundary of the series. Advantage has been taken of this approximate parallelism in estimating in advance the stress, time and number of cycles to be used in obtaining the experi-

mental points necessary to map out the various type 9 series presented in Figs. 15 to 19. By this means much time has been saved.

In the region of high corrosion-stresses in each series, the distances between adjacent graphs, for equal differences in corrosion-stress, are approximately equal. As the corrosion-stress is lowered, however, the effect of stress differences on the position of the type 9 graph becomes greater. As indicated in Fig. 15, decrease of corrosion-stress from 8000 to 7000 moves the type 9 graph outward about as far as does a decrease in corrosion-stress from 35,000 to 30,000. Change in position of the type 9 graph (as will be shown later) is in proportion to percentage change, rather than in proportion to actual change of corrosion-stress.

It is advantageous to view these type 9 graphs as originating in the time boundary. The course of each graph, then, as it extends to the left from the time boundary, represents the effect of increasing number of cycles in decreasing the time necessary to cause constant damage. Or the type 9 graph may be viewed as representing the effect of cycle frequency in accelerating penetration of metal under corrosion. As illustrated by Fig. 15, the lower the corrosion-stress, the higher the cycle frequency necessary to accelerate appreciably penetration of metal under corrosion.

The abruptness with which the type 9 graph turns to the left varies with the corrosion-stress. Graphs representing high corrosion-stresses curve to the left gradually; graphs representing lower corrosion-stresses leave the time boundary rather abruptly. For such a graph there is a fairly definite frequency limit above which corrosion pitting is greatly accelerated. Such a frequency limit may be called a "notching frequency" to correspond to the "notching stress" previously discussed in connection with the type 2 graphs. Notching frequency and notching stress are interdependent. Possible reasons for the abrupt acceleration of corrosion pitting when a certain combination of corrosion-stress and cycle frequency is exceeded are of considerable interest but cannot be discussed at this time.

As would be expected, the graphs in Fig. 15*b* are more distant from the origin than are the corresponding graphs in Fig. 15*a*. Distance of the type 9 graph from the origin increases with increase in the stress concentration; hence with increase in the depth and sharpness of pitting.

Type 9, *Constant-damage Series, Material IW*-14.5

The graphs shown in Figs. 9 to 15 inclusive were obtained with a nickel steel that had been quenched and tempered; the graphs shown in Fig. 16 were obtained with the same steel in the fully-annealed condition.

The two series shown in Fig. 16 represent corrosion conditions necessary to reduce the fatigue limit to 35,000 and 30,000, respectively. The

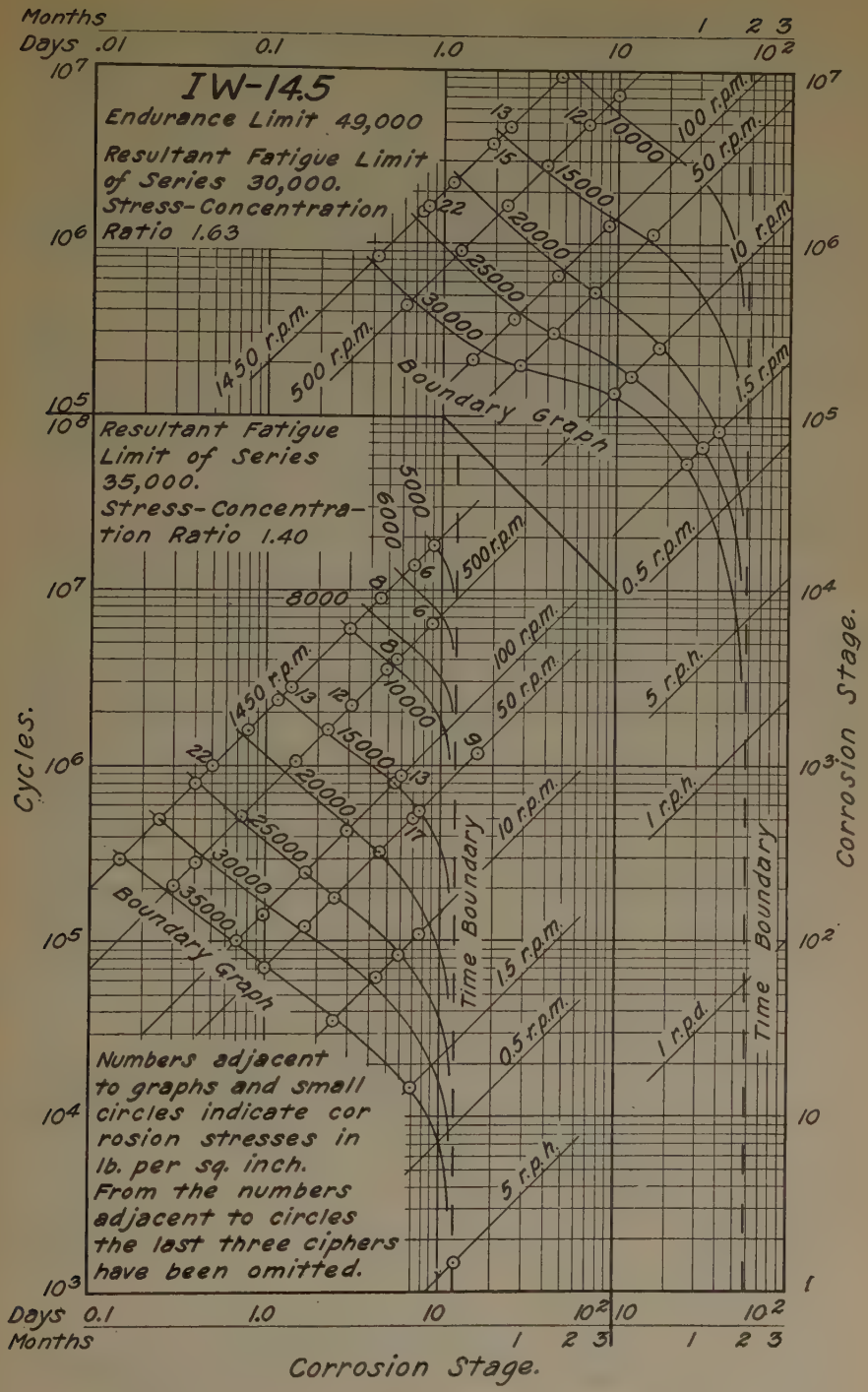

FIG. 16.—TYPE 9 CONSTANT-DAMAGE SERIES, ANNEALED NICKEL STEEL.

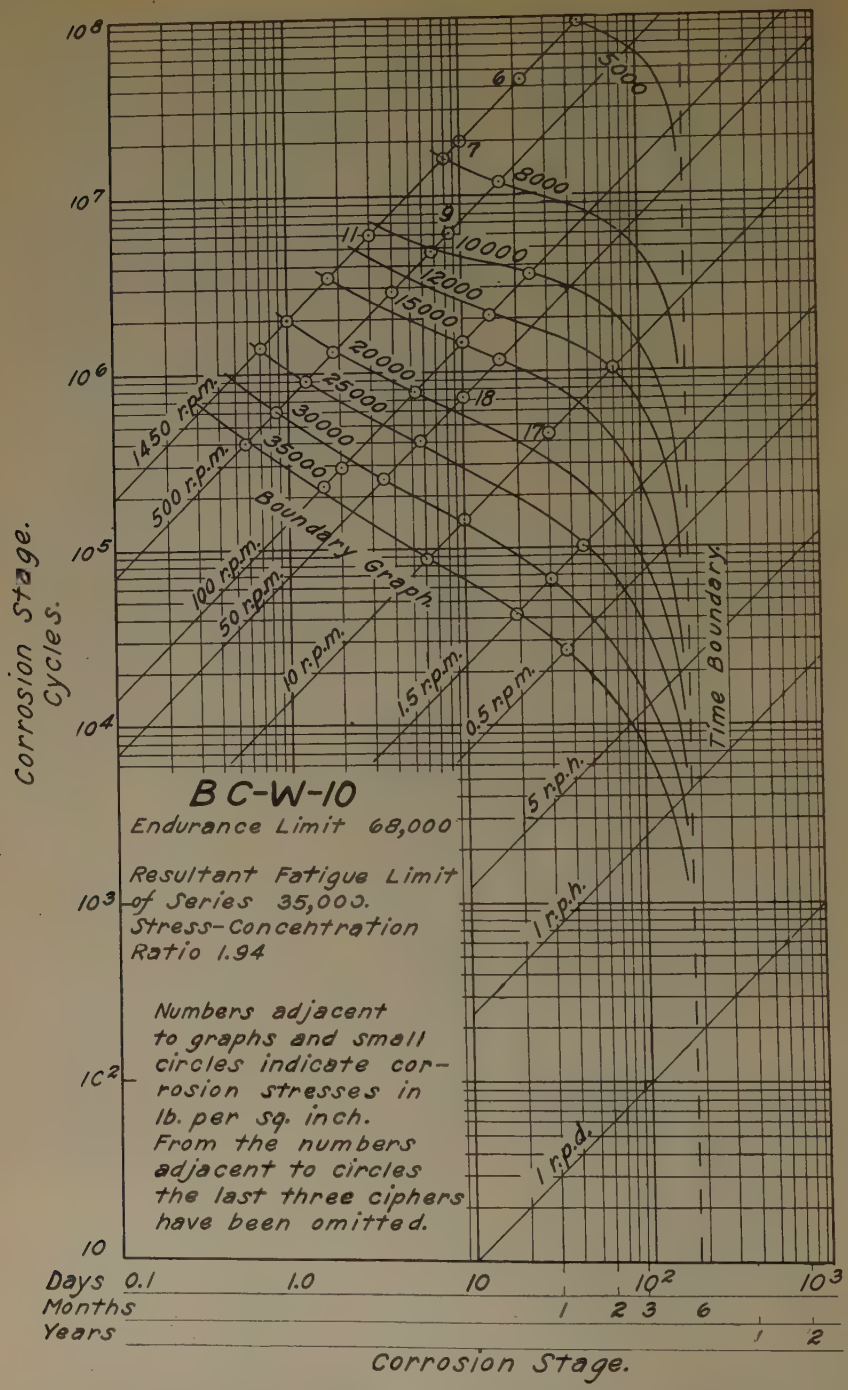

FIG. 17.—TYPE 9 CONSTANT-DAMAGE SERIES, CHROMIUM-NICKEL STEEL BC-W-10.

position of the time boundary for each series is accurately determined by means of the type 5 stressless-corrosion graph in Fig. 7.

The graphs in Fig. 16 are similar in form to the graphs in Fig. 15. The form of the type 9 graph, therefore, is evidently affected little by variation in physical properties due to heat treatment.

As would be expected, the graphs in the series at the right of Fig. 16 are farther from the origin of coordinates than are the corresponding graphs in the series on the left. The positions of the series in Fig. 16 should be compared with the positions of the series in Fig. 15 on the basis of equal stress-concentration ratios rather than equal resultant fatigue limits. The series in Fig. 15*a* and the series at the right of Fig. 16 represent nearly equal stress-concentration ratios. It will be observed that these two series differ only slightly in position. The position of the type 9 series for this nickel steel, therefore, is little affected by heat treatment.

Type 9, *Constant-damage Series, Material BC-W*-10

In Fig. 17 is shown a series of type 9 graphs obtained with a chromium-nickel steel that had been quenched and tempered. The physical properties of this steel are nearly the same as those of the nickel steel represented in Fig. 15.

Although the time boundary for the series represented in Fig. 17 has been determined as yet only approximately by extrapolation, the position of this time boundary has been located definitely enough to indicate the form of the type 9 graphs. These graphs are evidently similar in form to the graphs shown in Figs. 15 and 16. The position of the series represented in Fig. 17 may be compared with the position of the series represented in Fig. 15*b*, as the two series have nearly equal stress-concentration ratios. Comparison of these two series shows that they differ only slightly in position. This fact seems to indicate that for ordinary alloy steels the position of a constant-damage series depends chiefly on the stress-concentration ratio rather than on chemical composition.

Type 9, *Constant-damage Series, Material AY-W*-10

Two series obtained with another chromium-nickel steel of higher strength are shown in Fig. 18. The higher endurance limit and higher type 5 stressless-corrosion graph for this material have made it possible to use higher corrosion-stresses than those used in obtaining the five series represented in Figs. 15 to 17. These higher stresses have made it possible to extend the range of cycle frequencies down to a frequency of 5 per hour and to obtain noticeable effects at this low frequency.

The two series in Fig. 18 represent corrosion conditions necessary to reduce the fatigue limit to 45,000 and 40,000 respectively. The position of the time boundary for the series on the left has been determined

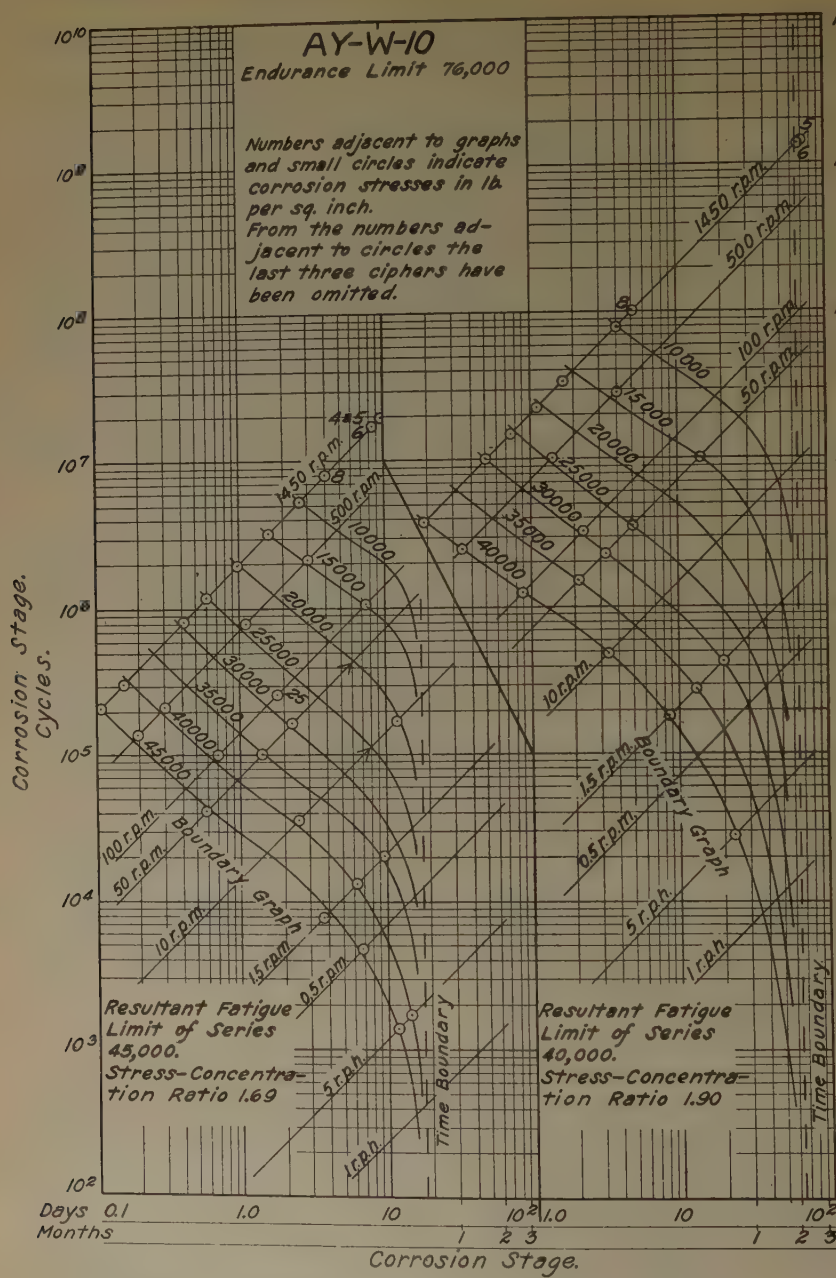

FIG. 18.—TYPE 9 CONSTANT-DAMAGE SERIES, CHROMIUM-NICKEL STEEL AY-W-10.

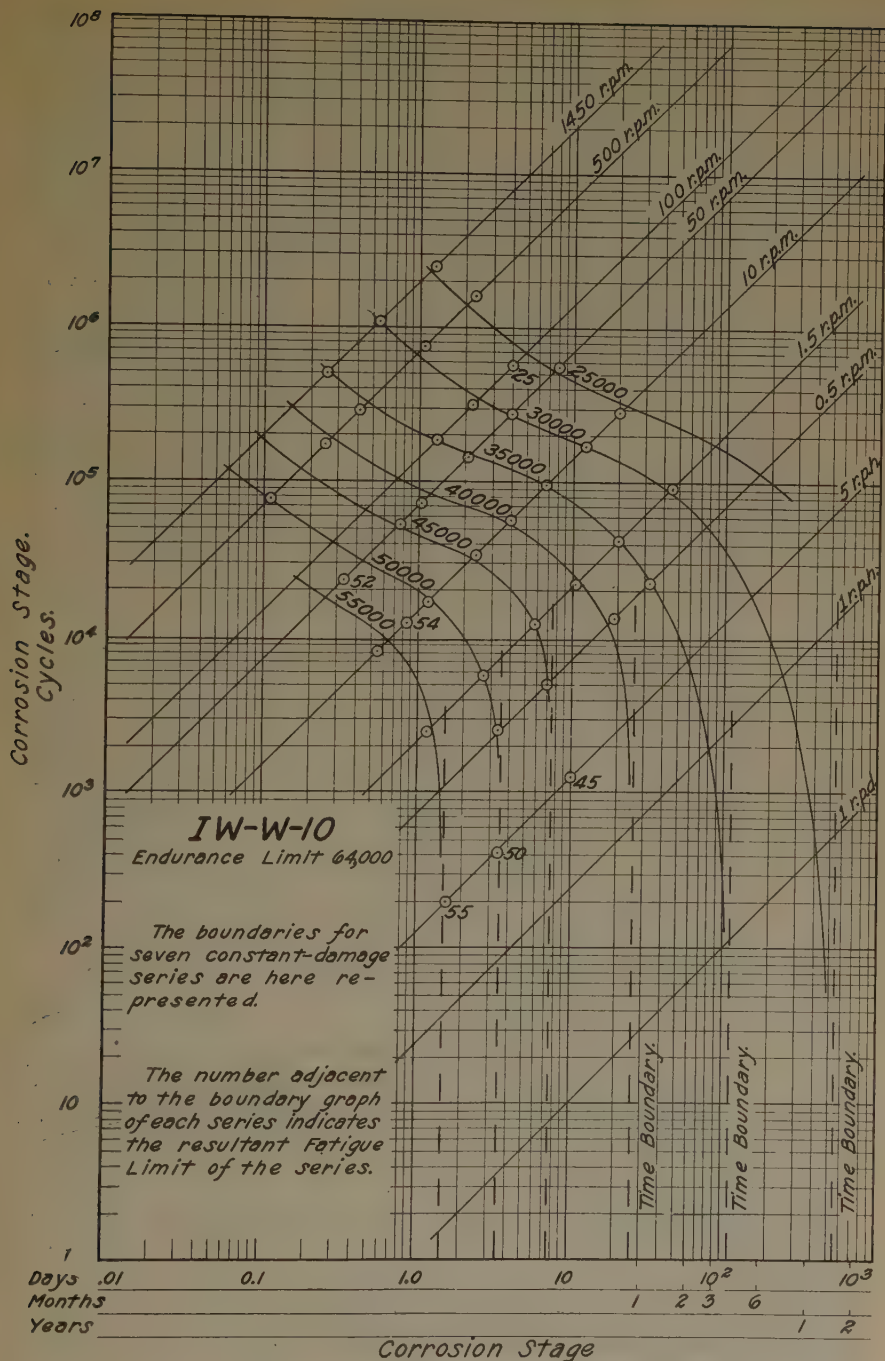

FIG. 19.—EFFECT OF VARYING BOUNDARY TIME ON FORM AND POSITION OF BOUNDARY GRAPH, TYPE 9.

definitely; the position of the time boundary for the series on the right has been determined as yet only by long extrapolation.

The form of the type 9 graph for this material is evidently nearly the same as for the materials represented in Figs. 15 to 17. The stress-concentration ratio for the series at the left of Fig. 18 differs only slightly from the ratios for the two series represented in Fig. 15*a* and at the right of Fig. 16. The stress-concentration ratio for the series at the right of Fig. 18 differs only slightly from the ratios for the two series represented in Fig. 15*b* and Fig. 17. Comparison of the positions of these series again leads to the conclusion that for ordinary alloy steels the position of the type 9 graph depends chiefly on stress-concentration ratio rather than on physical properties or chemical composition.

As shown in the series on the left of Fig. 18, corrosion-stress of 45,000 at a cycle frequency of 0.5 per min. decreases the corrosion time to less than one-half the boundary time. As shown in the series on the right of the figure, corrosion-stress of 40,000 at 5 cycles per hour reduces the corrosion time to less than one-half the boundary time. These results seem to indicate that repeated high stress range may greatly accelerate corrosion pitting even if the cycle frequency is less than 5 per hour.

Effect of Varying Boundary Time on Form and Position of Boundary Graph

The two positions of the constant-damage field shown in each of Figs. 15, 16 and 18 give some idea of the effect of varying boundary time on the form and position of the boundary graph. It seemed possible, however, that information of value would be obtained by determining for some one material a number of different positions of the constant-damage field. This has been done for material IW-W-10, and the positions of seven type 9 fields are represented in Fig. 19. Time is saved and confusion avoided by showing in this figure, for each position of the constant-damage field, only the boundary graph and time boundary.

On each boundary graph is marked the corrosion-stress, which necessarily is the same as the resultant-fatigue limit for this entire field. Two of the fields shown in this figure have been shown in Fig. 15. For the fields shown in Fig. 19 the boundary stresses range from 55,000 to 25,000. The boundary time corresponding to each boundary graph is obtained (in some cases by long extrapolation) from the type 5 stress-less-corrosion graph in Fig. 3.

The highest and lowest boundary stresses represented in Fig. 19 are approximately 86 and 40 per cent. of the endurance limit. Yet for all these series the boundary graphs are similar in form. The actually determined parts of these graphs are evidently not far from parallel. The extrapolated parts, therefore, have been drawn on the assumption that they remain not far from parallel.

In all these boundary graphs the effect of low cycle frequency is prominent. Cycle frequencies as low as 1.5 per min. have a noticeable

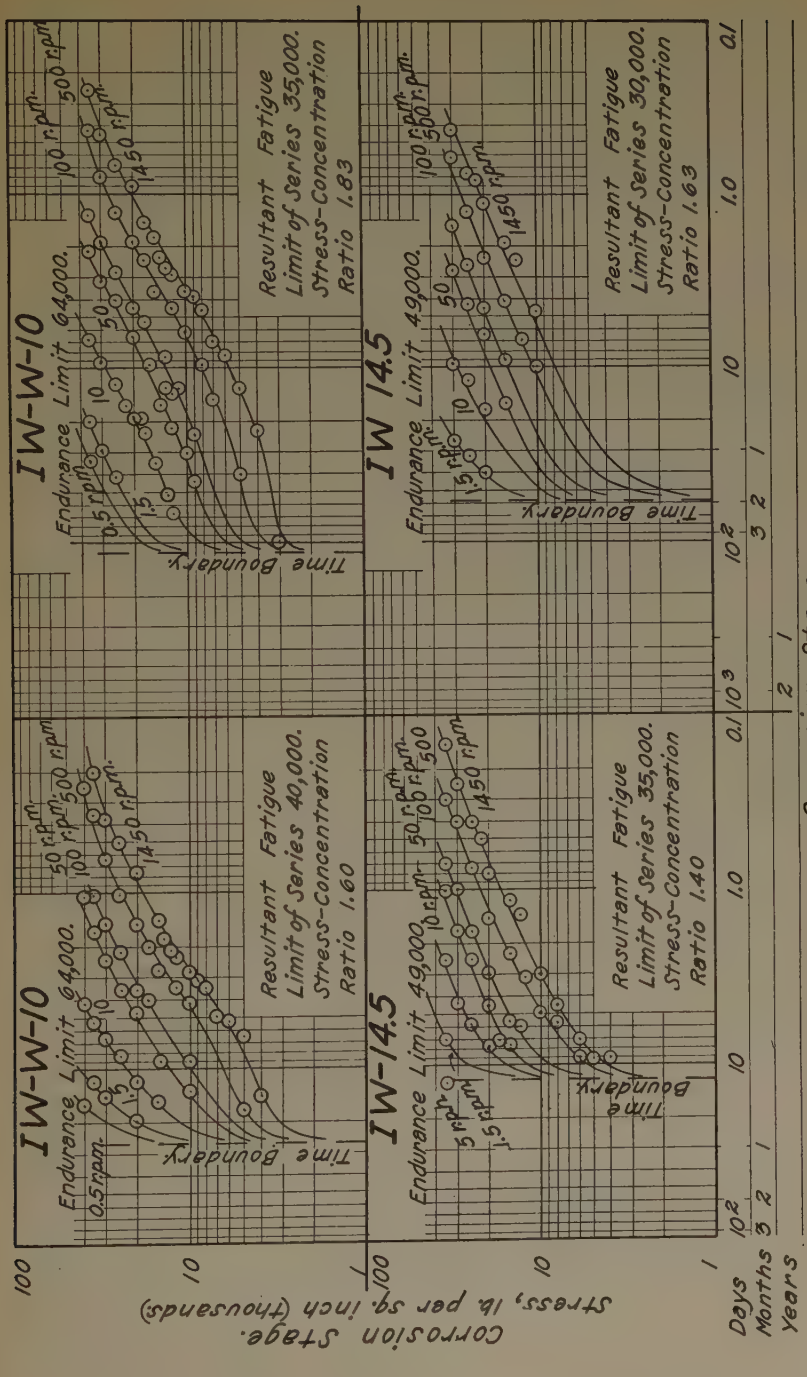

FIG. 20.—TYPE 6a CONSTANT-DAMAGE SERIES, NICKEL STEELS.

effect even in the short-time, highest stress graphs. In the graphs representing long boundary-time, the effect of low cycle frequency is especially prominent. The evidence seems to indicate, therefore, that the effect of cyclic stress on corrosion is not negligible in structures subjected to high stress range even of very low frequency. This tentative conclusion is supported by additional experiments to be described in Part VII.

Type 6 Graphs, Logarithmic Coordinates

In Figs. 20 and 21 are seven series of type 6 graphs representing the same materials that are represented in Figs. 15 to 18 by type 9 graphs. In Figs. 20 and 21, abscissas are measured from right to left. This unconventional arrangement is used so that each series together with the corresponding type 9 series (shown in Figs. 15 to 18) may represent two views of lines on a constant-damage surface. (Constant-damage surfaces on a logarithmic scale will be discussed later.) Each series in Figs. 20 and 21 is a type 6*a* series; that is, all the graphs of the series are on the same time scale, but each graph has its own cycle scale (not shown in the figures). The boundary stress in each type 6 series has the same significance as does the boundary graph of a type 9 series.

In drawing the graphs in Figs. 20 and 21, each series has been considered as a whole, and the graphs have been drawn to represent the most probable interrelationship for the entire series.

The impression obtained from a study of these seven series of graphs is that the typical form of the type 6 graph (except the portion distorted by influence of nearness to the time boundary) is a sloping, nearly straight line. In some of these series, the lines representing 1450 and 500 r.p.m. curve outward slightly as they approach the time boundary; in other series this curvature is absent. In some graphs, also, there is slight reversal of curvature as the graphs approach the boundary stress. This is probably due to the fact that the actual stresses represented by these parts of the graphs are not far from the endurance limit. Evidently the corrosion pitting is somewhat accelerated under these conditions.

The evidence seems to indicate, however, that the type 6 graph, as well as the type 9 graph, on a logarithmic scale is nearly straight, except as it approaches the time boundary. The relationship, therefore, between corrosion-stress and either time or number of cycles necessary to cause constant damage is exponential.

Basquin[11] called attention to the fact that for ordinary fatigue there is an exponential relationship between stress and number of cycles. Many ordinary fatigue graphs on a logarithmic scale consist of a straight, sloping line tangent at its lower end to a curve approaching a horizontal asymptote. As shown in Figs. 20 and 21, however, the type 6 graph gives

[11] O. H. Basquin: The Exponential Law of Endurance Tests. *Proc.* Amer. Soc. Test. Mats. (1910) **10**, 625.

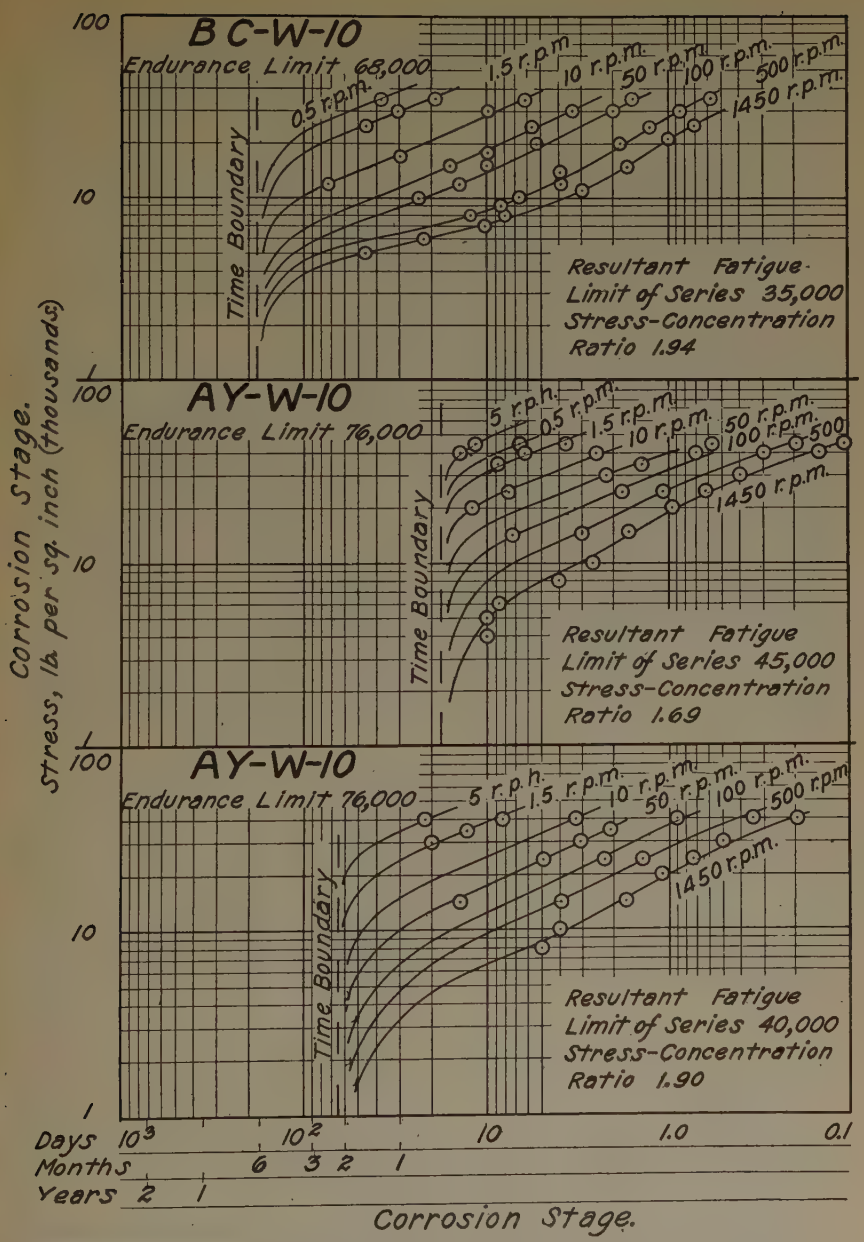

FIG. 21.—TYPE 6a CONSTANT-DAMAGE SERIES, CHROMIUM-NICKEL STEELS.

no clear evidence of approach to a horizontal asymptote. The exponential relationship between corrosion-stress and either time or number of cycles, therefore, may or may not indicate that the mutual action of corrosion and cyclic stress below the corrosion-fatigue limit is akin to fatigue.

For these type 6 graphs on a logarithmic scale, as well as for the previously described type 6 and type 9 graphs on a Cartesian scale, it is advantageous to view each series as starting from the time boundary. The course of each graph as it extends to the right, therefore, represents the effect of increasing corrosion-stress in decreasing the corrosion time necessary to cause constant damage.

As the graphs in Figs. 20 and 21 rise from their origin in the time boundary they turn to the right after reaching a height that becomes greater as the cycle frequency becomes lower. The abruptness with which the graphs turn to the right, however, is greater with higher cycle frequency. At high cycle frequency, the corrosion-stress corresponding to this abrupt turn is fairly definite. This limiting corrosion-stress, above which corrosion pitting is greatly accelerated, is another aspect of the notching stress that has been described in two previous papers[6,7] and in Part II of the present paper in connection with the type 2 graph. As shown in Figs. 20 and 21, the notching stress, for ordinary steels at least, increases with decrease in cycle frequency. With decrease in cycle frequency, however, the notching stress becomes less definite.

Constant-damage Surfaces, Logarithmic Coordinates

The complex relationship between the four variables under consideration is best studied by considering the type 9 series as the plan view and the corresponding type 6*a* series as the front view of a constant-damage surface. Each type 6*a* series in Figs. 20 and 21 represents a constant-damage surface as viewed from the "distant" end of the corresponding type 9 series (Figs. 15 to 18). The direction of view is parallel to the axis of cycles.

The constant-damage surface on a logarithmic scale (except as it approaches the time boundary) is evidently a nearly plane surface, sloping diagonally downward as it recedes from the imagined vertical axis of corrosion-stresses. As it approaches the time boundary, the constant-damage surface curves abruptly downward and approaches the vertical time-boundary plane as an asymptote. The stress-time-cycle relationship for constant damage, therefore, is an exponential relationship except when conditions are such that the damage is due chiefly to stressless corrosion. These conclusions apply to ordinary alloy steels. It seems probable that they apply also to carbon steels in view of the fact that the notching stress (as illustrated by type 2 graphs in Fig. 1) for carbon and for ordinary alloy steels is practically the same.

For ordinary alloy steels, and probably for carbon steels, the position and angle of slope of the nearly plane part of the constant-damage surface are apparently affected only slightly by variation in chemical composition and physical properties. For corrosion-resistant steels no definite conclusions can be drawn at this time.

Part VI—Constant Net-damage Graphs and Surfaces

Total Damage and Net Damage

The damage due to corrosion under cyclic stress, as measured by lowering of the fatigue limit, may be resolved into two parts. The total damage consists of the damage due to stressless corrosion plus the excess or net damage due to the cyclic stress. The relation between total damage and net damage is illustrated by any of the series of type 5 graphs in Figs. 3 to 8. In Fig. 3, for example, the damage due to stressless corrosion is measured by the distance of the stressless-corrosion graph below its origin, which represents by ordinate the endurance limit. In the same figure, the total damage due to corrosion under cyclic stress of 4000 is measured by the distance of the graph representing this corrosion-stress, below the origin, which represents the endurance limit. The differential or net damage, due to corrosion-stress 4000, is measured by the distance of the graph representing this stress below the stressless-corrosion graph. The ratio of net damage to total damage evidently varies with corrosion time.

For carbon and ordinary alloy steels the damage due to stressless corrosion is a relatively large part of the total damage. For such metals, the net damage under some conditions of stress, time, and number of cycles is a very small part of the total damage. For corrosion-resistant metals, the type 5 stressless-corrosion graph would evidently be nearly horizontal. The net damage, therefore, for such metals is a large proportion of the total damage. For some metals under mild corrosion conditions the net damage is practically the total damage.

Constant Net-damage Graphs

The stress-time-cycle relationship for constant net damage is of theoretical and practical importance. By "constant net damage" is meant a constant percentage lowering of the fatigue limit below the fatigue limit that would result (in the same length of time) from stressless corrosion alone. Constant net damage, therefore, means constant percentage elevation of the stress-concentration ratio above the ratio that would result in the same time from stressless corrosion alone. To obtain a constant net-damage graph a line is drawn below the stressless corrosion line in a type 5 series, so that the ordinate of each point in the new line is a constant percentage of the ordinate of the corresponding point in

the stressless-corrosion line. The coordinates of the intersections of the new line with the type 5 graphs are used in plotting graphs to represent the stress-time-cycle relationship for constant net damage.

Type 10 *Constant Net-damage Graphs, Logarithmic Coordinates*

The type 10 graph is similar, in arrangement of coordinates, to the type 9 graph. In Figs. 22 and 23 are shown four series of type 10 graphs representing the same four steels that are represented by type 9 graphs in Figs. 15 to 18.

It will be observed that the scatter of experimental points in these type 10 graphs is greater than in the corresponding type 9 graphs. The reason for this will be discussed in connection with the type 11 graphs to be described later. In spite of the wide scatter of experimental points, each series as a whole gives clear indication of the form and direction of the representative type 10 graph. No attempt, however, has been made to draw interpretative graphs. The experimental points have been merely connected by straight lines.

The type 10 graph of ideal form, on a logarithmic scale, is evidently a nearly straight line. For this graph there is no time boundary and no clear indication of approach to an asymptote. The angle between the type 10 graph and the axis of abscissas is evidently less than the corresponding angle between the type 9 graph and the same axis. Some of the graphs in Figs. 22 and 23 are nearly parallel to the axis of abscissas. If such graphs were representative, it would lead to the conclusion that the net damage due to cyclic stress is independent of time. The representative type 10 graph for these steels, however, makes a slight angle with the axis of abscissas. Time, therefore, is a factor in the net damage due to cyclic stress, but it is a less influential factor in net damage than in total damage or in the damage due to stressless corrosion.

It is advantageous to consider each series of type 10 graphs as the plan view of a constant net-damage surface. Each series, therefore, should be studied in connection with front and side views of this surface.

Type 11 *Constant-damage Series, Logarithmic Coordinates*

The type 11 graph is similar, in arrangement of coordinates, to the type 6 graph. In Fig. 24 are shown four series of type 11 graphs representing the same steels that are represented by type 10 graphs in Figs. 22 and 23. The four series shown in Fig. 24 are type 11*a* series, in which abscissas for all graphs represent the same time scale but each graph has its own cycle scale (not shown in the figure).

The scatter of experimental points is much less for the type 11 than for the type 10 graphs. The type 11 graph, like the type 10 graph, is evidently a nearly straight line showing no approach to a horizontal asymptote. The graphs for each series in Fig. 24 have been drawn as

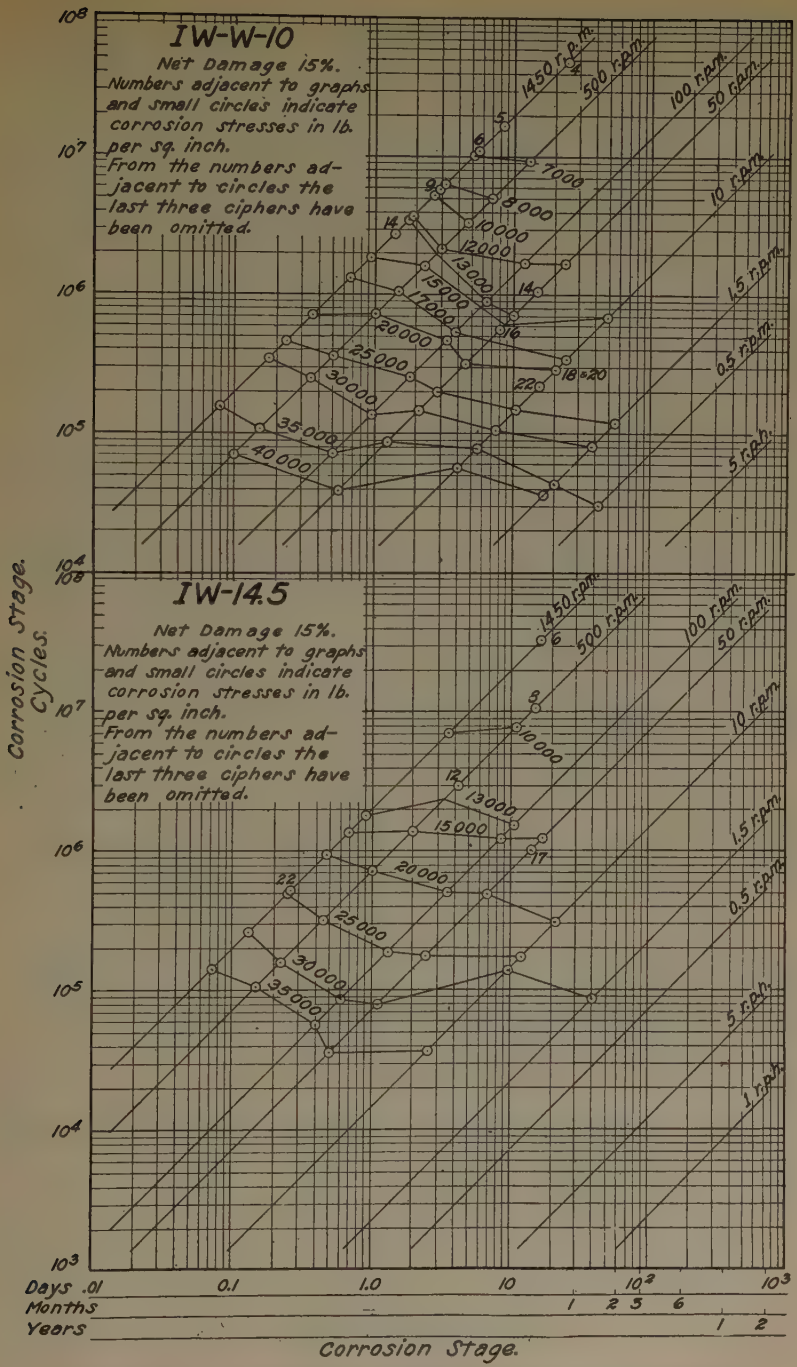

FIG. 22.—TYPE 10 CONSTANT NET-DAMAGE SERIES, NICKEL STEELS.

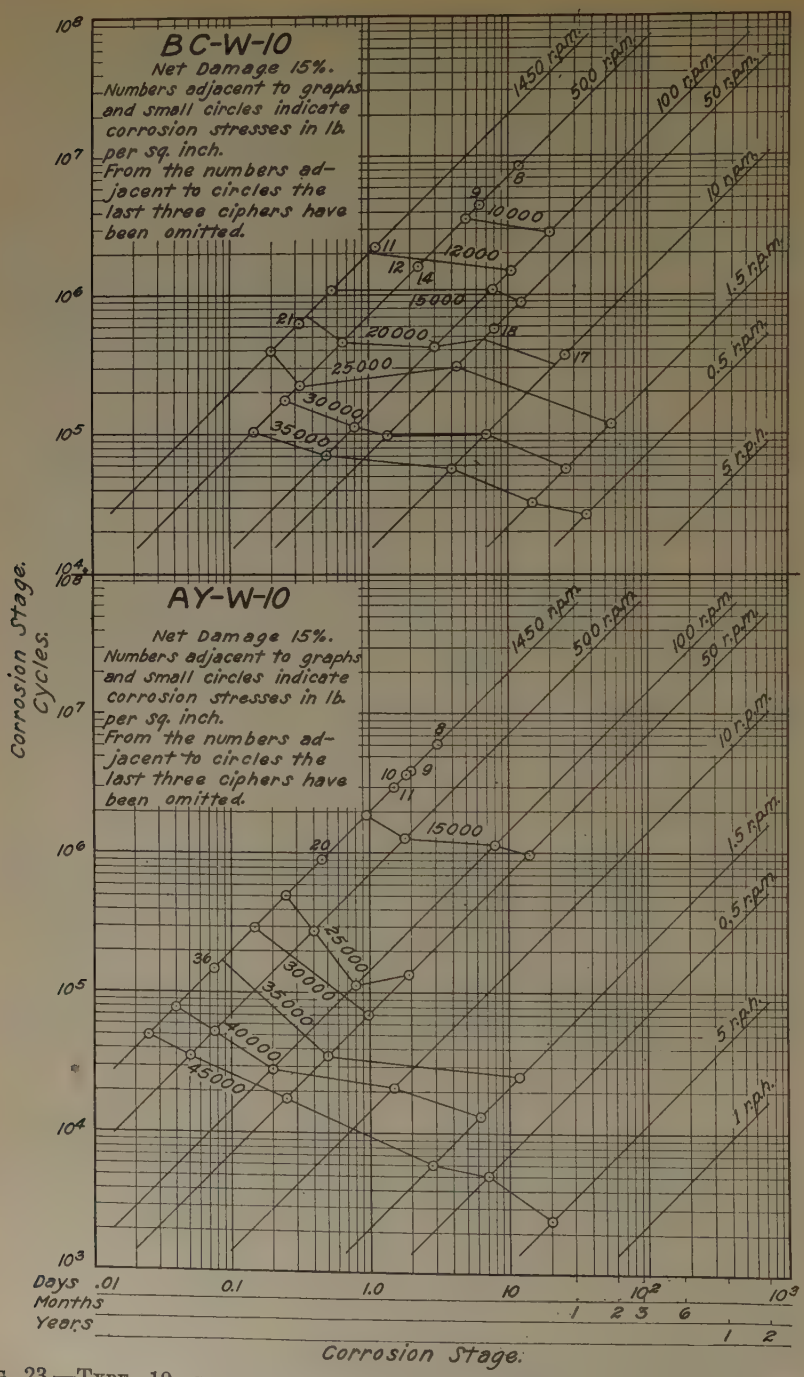

FIG. 23.—TYPE 10 CONSTANT NET-DAMAGE SERIES, CHROMIUM-NICKEL STEELS.

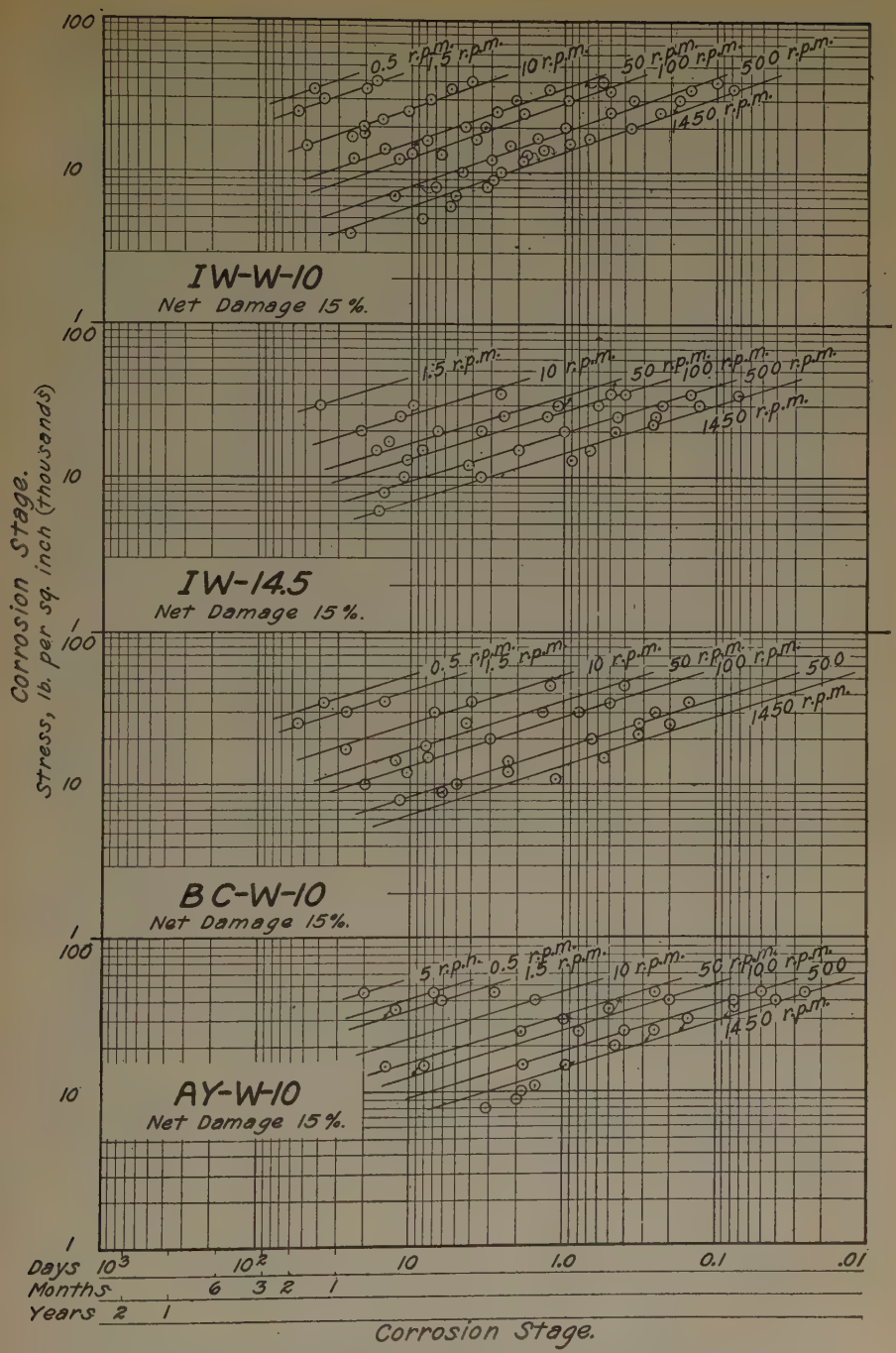

FIG. 24.—TYPE 11 CONSTANT NET-DAMAGE SERIES, VARIOUS STEELS.

straight parallel lines. Such lines best represent the series as a whole. Not only are the lines throughout each series parallel but the lines of all four series are not far from parallel. The angle between the type 11 graph and the axis of abscissas is evidently much less than the corresponding angle between the type 6 graph and the axis of abscissas.

Constant Net-damage Surfaces

Each Type 11*a* series represented in Fig. 24 may be considered as the front view of a constant net-damage surface, of which the corresponding type 10 graph is the plan view. The type 11*a* series represents this surface as viewed from the distant end of the corresponding type 10 series; the view is in a direction parallel to the axis of cycles. A type 11*b* series would represent a side view of the surface. As the type 11*b* series was found to be similar to the type 11*a* series, the former has been omitted.

As indicated by the two views of each of the four surfaces represented in Figs. 22 to 24, the constant net-damage surface on a logarithmic scale is a nearly plane surface. The slope of this surface is considerably less than the slope of the nearly plane part of the constant total-damage surface. This explains why the scatter of experimental points is greater in a type 10 series than in the corresponding type 9 series.

For ordinary alloy steels and probably for carbon steels, therefore, the stress-time-cycle relationship for constant net damage is an exponential relationship, which extends over a wide range of stress, time and number of cycles. For these steels the constant net-damage surface shows no evidence of approach to a horizontal asymptote within the time range investigated. With further extension of the time range it is possible that the graphs may curve outward at very low stresses. For more corrosion-resistant material, for which the notching stress corresponds to a definite pitting limit, the constant net-damage surface may possibly approach a horizontal asymptote. Evidence for this is at present lacking.

Extrapolation of the type 10 and type 11 graphs shown in Figs. 22 to 24, assuming that the straight-line relationship continues, confirms the conclusions expressed in Part V, that cyclic stress even of very low frequency may have considerable effect in accelerating corrosion pitting. Even low corrosion-stresses, moreover, acting over a long period of time, may have appreciable effect in increasing the penetration of metal under corrosion.

Part VII—Stress-time-cycle Relationship for Other Corrosion Conditions and for Other Metals

Effect of Steady and Intermittent Tensile Stress on Corrosion

That steady tensile stress accelerates corrosion of some non-ferrous metals is well known. "Season cracking" under internal tensile stress

is an example. Experiments by Parr and Straub[12,13] seem to indicate that, for steel in contact with hot solutions of caustic soda, chemical attack is somewhat accelerated by steady tensile stress. This suggests the possibility that even at room temperature the corrosion of steel in contact with water may be accelerated by steady stress. The experiments described below were made to investigate the effect of steady and intermittent tensile stress on corrosion of steel in contact with water at room temperature.

A silicon-nickel steel (material HG-0-7.5) of spring temper, which has been discussed in previous papers,[4] was used in these experiments. The composition, heat treatment and physical properties of this steel are given in Tables 1, 2 and 3. The water used in these experiments was the carbonate water used throughout the previously described investigation.

To compare the effect on corrosion of steady and intermittent tensile stress, standard tension test specimens of this steel in contact with water were stressed in an ordinary tension-testing machine. Under steady tensile stress, specimens failed quickly if the tensile stress exceeded about 175,000 lb. per sq. in. At lower steady stresses, specimens did not fail even after several weeks' exposure. Specimens of the same steel in contact with water were subjected to intermittent tensile stress, with frequency of one cycle per hour. The tensile stress was maintained for ½-hr. intervals and released every alternate ½ hr. Under these conditions, specimens failed as follows: Stress 150,000, time 25 hr.; stress 120,000, time 96 hr.; stress 115,000, time 150 hr. The breaking strength of this steel under intermittent stress with frequency of one cycle per hour, therefore, was about 115,000. Evidently the effect of intermittent high tensile stress, even of very low cycle frequency, is much greater than the effect of steady tensile stress.

The experiments described do not exclude the possibility that steady high tensile stress has some effect on corrosion. To investigate this subject additional experiments were made. Specimens were subjected to stressless corrosion in carbonate water for 10 or 11 days. They were then oiled and subjected to intermittent tensile stress in air, with frequency of one cycle per hour. For specimens so tested the breaking stress was 200,000 to 205,000. Experiments have not yet been made to determine the effect of stressless corrosion followed by steady tensile stress. The stress-concentration ratio caused by stressless-corrosion pitting of such material, however, is at least 1.7. Under steady tensile stress nominally 200,000, therefore, the actual stress in the bottoms of corrosion pits would be above the tensile strength of the material. For

[12] S. W. Parr and F. G. Straub: The Cause and Prevention of Embrittlement of Boiler Plate. *Proc.* Amer. Soc. Test. Mats. (1926) **26**, Pt. II, 52.

[13] S. W. Parr and F. G. Straub: Embrittlement of Boiler Plate. *Proc.* Amer. Soc. Test. Mats. (1927) **27**, Pt. II, 52.

this and other reasons, it is believed that after stressless corrosion the breaking stress under steady tension would be not far above 200,000. The breaking strength after stressless corrosion was higher by about 25,000 or 30,000 than was the breaking strength under simultaneous corrosion and steady stress of about 175,000. The effect of steady stress of 175,000 on corrosion, therefore, is much less than the effect of intermittent stress of 115,000 with frequency of only one cycle per hour.

Mention has been made of a boiler that failed in 1926 at the Naval Engineering Experiment Station under the influence of combined stress and corrosion. The boiler head failed at the knuckle, where there was no seam. The water used in the boiler was the same carbonate water used throughout this investigation. No boiler compound was used. This boiler had been used about 1100 times in 11 years. In view of the evidence presented in this paper it seems unquestionable that the intermittent stress with frequency only about 100 cycles per year had considerable influence in accelerating the corrosion of this boiler and thus causing failure.

Effect of Varying Corrosion Conditions on Form and Position of Constant-damage Graphs and Surfaces

A few experiments have been made with nickel steel, material IW-W-10, in salt water. These experiments indicate, as might be expected, that a type 9 constant-damage series obtained with salt water is nearer to the origin of coordinates than the corresponding series obtained with fresh water. By increase in the intensity of corrosion, therefore, the constant-damage surface is moved downward and inward. Whether the form of the constant-damage surface is much changed by variation in corrosion intensity has not yet been determined. If the form and slope of the constant-damage surface are not greatly changed by change in corrosion intensity, it may be possible to investigate the stress-time-cycle relationship for any given corrosion condition by means of relatively few experiments.

Constant-damage Graphs for Corrosion-resistant Steels and for Non-ferrous Metals

As shown in previous papers,[6,7] for corrosion-resistant steels, and for corrosion-resistant non-ferrous metals such as monel metal, the corrosion-fatigue limit, determined at a cycle frequency of 1450 r.p.m., corresponds to a fairly definite notching limit. Below this limit, pitting is so slight as to be almost negligible. For such material the corrosion-fatigue limit is more definite than for metals that are deeply pitted by stressless corrosion. For such metals, moreover, the notching limit (corrosion-fatigue limit) is possibly less influenced by cycle frequency than for ordinary steels. The corrosion-fatigue limit for a corrosion-resistant

material, therefore, is probably the most important index of its behavior under corrosion and cyclic stress. Nevertheless it is of theoretical, as well as of some practical, importance to know for such alloys the form and position of the constant-damage graphs and surfaces.

In obtaining constant-damage graphs for corrosion-resistant alloys, the field of investigation is evidently limited to stresses between the corrosion-fatigue limit and the endurance limit, as below the corrosion-fatigue limit pitting is negligible. Investigation is now under way to determine constant-damage graphs and surfaces for corrosion-resistant steels and non-ferrous metals. A few experiments with stainless iron and with monel metal indicate, as was expected, that for these two metals the type 9 constant-damage series is further from the origin of coordinates than for ordinary steels. Increase in corrosion resistance, therefore, moves the constant-damage surface outward and upward.

The forms of the constant-damage graphs and surfaces for corrosion-resistant metals have not yet been determined. As, for such alloys, the effect of stressless corrosion is slight, net damage due to cyclic stress is a large part of the total damage. Constant-damage graphs for corrosion-resistant steel, therefore, may possibly resemble somewhat the constant net-damage graphs for carbon and ordinary alloy steels. Definite conclusions about this, however, must await the results of experiment.

Summary

This paper discusses the interrelationship of stress, time, and number of cycles in causing penetration of metals under corrosion. The resultant fatigue limit is used as a criterion of the depth and sharpness of corrosion pitting. Four variables and their interrelationship, therefore, are considered.

The paper first discusses the relationship between corrosion-stress and resultant fatigue limit with the other two variables held constant. The form of the type 2 graph, representing this relationship, indicates local strengthening of the metal at the bottoms of the corrosion pits. The field of investigation is then extended to include stresses between zero and the endurance limit.

By thus widening the range of corrosion-stresses it was then possible to extend the range of cycle frequencies so as to include frequencies as low as 5 cycles per hour. "Constant-damage" graphs were then developed so as to represent the stress-time-cycle relationship with resultant fatigue limit held constant. Constant-damage series of graphs are discussed as various views of constant-damage surfaces. Constant-damage graphs and surfaces on a logarithmic scale are found to be the most useful method of representing the relationship between the four variables. Graphs for alloy steels varying widely in composition and physical properties are discussed. From the type 5 graphs, other

graphs and surfaces are developed to represent the damage (due to cyclic stress) in excess of the amount of damage that would be caused by stressless corrosion alone.

The paper discusses the effect of steady and intermittent tensile stress on corrosion, also the stress-time-cycle relationship as affected by varying corrosion conditions, also the stress-time-cycle relation as it affects the corrosion of corrosion-resistant steels and non-ferrous metals.

Acknowledgments

Acknowledgment is due to the following personnel of the Naval Engineering Experiment Station: to Capt. H. C. Dinger, U. S. N., Officer in Charge, and Lt. Comdr. G. K. Weber, U. S. N., Test Officer, for encouragement received in this investigation; and to George F. Wohlgemuth, and Lawrence Thompson, Associate Metallurgists; W. C. Stewart, Assistant Metallurgist; W. E. Harvey, Junior Metallurgist; A. P. Vandermast and Donovan Lawless, Laboratorians; and John K. Amoss, Quarterman Machinist, for assistance in the investigation.

Acknowledgment is also due to the International Nickel Co. and the American Rolling Mill Co. for generous cooperation by supplying material.

[Turn to page 53 for discussion of this paper.]

Corrosion of Tin and Its Alloys

By C. L. Mantell,* New York, N. Y.

(New York Meeting, February, 1929)

Although so common and well known a metal, tin is really a less abundant element than many of those less familiar and usually ranked with the scarce or rare elements, such as cerium, yttrium, lithium, beryllium, titanium, zirconium and vanadium.

The color of tin is white, with a slightly bluish tinge. When it is compared with nickel, the latter metal is brown. When placed alongside of tin, chromium is definitely blue. Tin is whiter than silver or zinc. Exceedingly thin films of tin show various shades of brown by transmitted light. The metal has a brilliant luster, and when mirror-polished, has high light reflectivity. The luster depends to a large extent upon the pouring temperature at which the metal is cast. If the temperature be too high, iridescent colors may show on the surface. These are the result of oxide film formation. If the pouring temperature be too low, the surface is dull. Small amounts of foreign metals, such as lead, arsenic, antimony and iron, decrease the luster of tin and impart a yellowish tinge to the metal.

The structure is decidedly crystalline. The cast metal is a mass of crystals. When a bar of tin is bent, it emits a characteristic creaking sound. This is called the "cry" of tin, resulting from the grinding of the crystals one against the other during the bending of the metal. Tin metal may lose its crystalline structure by cold working, but grain growth occurs rapidly under the influence of heat. Metal which has been cast at a low temperature may become amorphous as the result of mechanical work. If such material be heated to temperatures well below the melting point, say at 110° C. for a half hour or for a few minutes at 150° C. recrystallization occurs. If the surface of tinned plate, tin foil, or tin metal in cast form be etched with hydrochloric acid containing a little free chlorine, attack occurs at the intercrystalline faces. The surface shows patterns resembling the frost flowers on window panes in winter. The etched appearance is called *moiré metallique*. Fine dendritic surface crystals of tin may be obtained by casting the metal on a surface of polished steel. In commercial tin plate, the intercrystalline boundaries are shown by fine grooves or channels, which result from the method

* Consulting Engineer, Pratt Institute.

of manufacture, during which the plates are drawn from a bath of molten tin and allowed to drain. More fusible impurities are forced, by the crystallization of the tin, to the intercrystalline junctions, after which the still fluid impurities drain off, leaving minute channels. The fine grain structure obtained by quenching molten tin in water is not affected by annealings over long periods at temperatures below the melting point. If, however, so-called "block tin" has its crystalline structure extremely subdivided by severe compression, it can be caused to recrystallize at 150° C. Tin crystals sometimes show lines which are due to stresses set up during rapid growth.

Cold-rolled tin immediately after rolling shows a tendency to recrystallize at ordinary temperatures. If annealing be carried out at 170° C. to 180° C., secondary recrystallization occurs. In this case the smaller crystals grow at the expense of their neighbors. The resulting metal has a very coarse crystalline structure. If rolled once again and allowed to stand, the primary crystals which form are larger than before, but about the same size as those produced by annealing at temperatures up to 150° C.

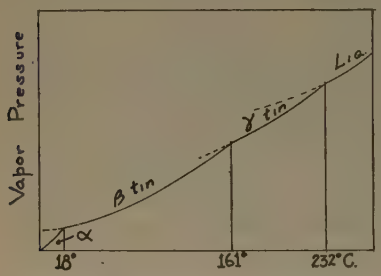

FIG. 1.—EQUILIBRIUM DIAGRAM OF THE ALLOTROPIC FORMS OF TIN; α, CUBIC; β, TETRAGONAL.

Single crystals of tin have been made by a number of investigators. Mark and his co-workers[1] found that when a tin crystal is elongated to a wire and heated at 150° C. for 3 min., the wire is disrupted by recrystallization which begins at the ends, growing at the rate of approximately 1 mm. per sec. The orientation of the new crystal in reference to the old one is such that the width of the wire is not changed on elongation. Tammann and Mansuri[2] state that coalescence of the grains of powdered tin occurs by recrystallization at 142° C.

Tin exists in a number of allotropic forms. These are shown diagrammatically in Fig. 1. At low temperatures the stable form is gray cubic or alpha tin, which changes at 18° C. to ordinary white tetragonal or beta tin. This suffers transposition at 161° C. to the so-called rhombic brittle or gamma tin, which at 232° C. passes into the molten state. Von Simson[3] states that according to his X-ray studies, gamma tin is hexagonal.

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[1] M. Polanyi and E. Schmid: Verfestigung und Entfestigung von Sn-Kristallen. *Ztsch. für Physik* (1925) **32**, 684.

[2] G. Tammann and Q. A. Mansuri: Zur Rekristallisation von Metallen und Salzen. *Ztsch. anorg. Chem.* (1923) **126**, 119.

[3] Cl. v. Simson: Röntgenuntersuchungen an Amalgamen. *Ztsch. physikal. Chem.* (1924) **109**, 183.

Bijl and Kolkmeijer[4] show from their X-ray studies of gray tin that it crystallizes in the cubic system. Its space-lattice is of the diamond type, with an edge of unit cube $a = 6.46$ Å units.

Tin metal is soft. It can be readily cut with a knife, but when filed it chokes the teeth of the tool. On the von Moh scale, it shows a hardness of 1.8, as compared to 1.5 for lead and 2.5 for gold. The metal is slightly hardened by hammering.

Tin is most ductile in the neighborhood of 100° C. At about 200° C. it can be pulverized in a mortar. Its tensile strength is low, being about 1 ton per sq. in. When bars of tin are subjected to repeated bending, heating of the metal occurs as the result of friction of the crystals.

The electrical conductivity of tin is about one-seventh that of silver. The electrical resistance varies considerably with temperature. The resistance of tin decreases normally with falling temperature down to −269.2° C., or 3.8° K., when the resistance suddenly becomes immeasurably small and the metal becomes an excellent conductor. Tin shows marked volume changes during melting or freezing. Conversely, the specific volume of tin varies markedly with temperature, and the fluidity increases in an almost parallel line.

Chemical Properties of Tin

Tin metal is not affected by hydrogen. Considerable work in the literature seems to indicate the possibility of the occurrence of tin hydrides but if they be formed, they are very readily decomposed. The metal is but little affected by air at ordinary temperatures, even in the presence of moisture, but gradually acquires a superficial tarnish. Tammann[5] estimated that to form the first visible layer of oxide coating on tin metal in dry air would take 36×10^8 years. Tin is readily oxidized by air at elevated temperatures, with the formation of its oxides. When the metal is heated to near its boiling point, it burns in air with a pale, white flame. At ordinary temperatures it is appreciably affected by moist oxygen. In this section we will attempt to confine ourselves to the purely chemical reactions of tin and discuss its corrosion in more detail elsewhere. The halides unite directly with tin, forming stannic salts. Dry chlorine reacts with tin at room temperatures, as shown in commercial detinning.[6] Fluorine does not react with tin at low temperatures, but at 100° C. it forms stannic fluoride. Tin is feebly attacked by hydrofluoric acid, slowly dissolved by dilute hydrochloric and rapidly by hot concentrated hydrochloric acid, with the formation of stannous

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[4] *Chem. Weekbl.* (1918) **15**, 1264; *Proc.* Acad. Amsterdam (1919) **21**, 405, 494, 501.

[5] *Rec.* Trav. Chim. Pays-Bas (1923) **42**, 547.

[6] C. L. Mantell: Utilization of Chlorine in Recovery of Tin and Tin Salts from Tin Plate Scrap. *Trans.* Am. Electrochem. Soc. (1926) **49**, 267.

chloride and the evolution of hydrogen. The reaction is accelerated by the presence of small amounts of platinic chloride, or when tin is in contact with copper, silver, lead, or platinum metal. Hot hydrobromic or hydriodic acid also readily dissolves tin. Alkali hypochlorites react on tin, forming an oxychloride with the evolution of oxygen.

Tin unites directly with sulfur when a mixture of the two elements is heated. Hydrogen sulfide does not act readily on tin at ordinary temperatures, but at 100° C. to 400° C. it forms stannous sulfide. Over appreciable time periods, hydrogen sulfide tarnishes tin. Ammonium sulfide attacks tin more readily than does hydrogen sulfide. When tin is fused with sodium sulfide, stannous sulfide is formed. Sulfuryl chloride and sulfur monochloride, S_2Cl_2, both attack tin. Sulfur dioxide reacts with the metal with the formation of stannous sulfide. Dilute sulfuric acid does not readily react on tin in the cold, but the action is accelerated by the presence of oxygen. Tin reacts vigorously with selenium and tellurium when a mixture of the two is heated.

Tin does not form a compound by direct union with nitrogen. It is oxidized by hot nitric acid to hydrated stannic oxide or stannic acids.

The soluble salts of tin are few. Those which are commercially important are the chlorides, acetates, sulfates and oxalates. All of them show tendencies to hydrolyze. Tin in its compounds is amphoteric.

The physiological action of tin has been the subject of widespread study. The number of authentic cases wherein tin and its salts have been poisonous is very low, being almost nonexistent. The stannous salts are believed to be only very slightly toxic, but the stannic salts somewhat more so, according to Vaubel. The rarity of tin poisoning, contrasted with the extended use of the metal for cooking vessels and in tin cans for preserving food, shows that the attendant risks are very small indeed. There are no special pharmaceutical preparations of tin or its compounds.

Physical Corrosion—Tin Pest

Tin is one of the few metals which have sufficient dignity to be subject to a "disease." Many workers have observed that ordinary tin changes into a gray powder when exposed to extremes of cold. Medallions, coins and antiques in museums acquire a surface crust of powdery gray tin which gradually grows, seemingly self-catalyzed, until complete disintegration results. This is the so-called "tin pest" or "disease" of the museums. Krause[7] states that Aristotle[8] refers to the change tin undergoes when subjected to extreme temperatures. Erdman,[9] in 1851, noted structural changes in organ pipes. He thought them to be the

[7] E. Krause: Die Metamorphosen des Zinns. *Prometheus* (1900) **11**, 701.
[8] De Mirabilibus Aucultationibus.
[9] *Jnl. prakt. Chem.* (1851) (1), **52**, 428.

effect of vibration. Fritzsche[10] described the disintegration of pig tin. After exposure to the Russian winter of 1867–8, when the temperature during January fell as low as −38° C., some blocks of Banka tin had disintegrated to granular crystalline pieces and coarse powder. A large number of workers have noted the same effect. Gowland[11] refers to the change in an old vessel consisting of 94.35 per cent. tin, 5.06 per cent. lead, traces of iron and copper, 0.59 per cent. oxygen and carbon dioxide in the following words:

"The extraordinary molecular change which the metal of this vessel has undergone is of more interest to the physicist and metallurgist than to the antiquary. The metal is not much oxidized, yet it is so exceedingly brittle that it can be easily broken with the fingers. The effect of time upon it has resulted in a complete alteration of its molecular structure, the mass of the alloy being converted into an agglomeration of crystals, and to this its brittleness is due. On smelting and casting a small fragment, it is found that the crystalline structure disappeared and the metal regained its original toughness."

When tin or a tin alloy is affected by tin pest, gray-colored spots appear and the metal becomes quite brittle. Expansion occurs so that the product occupies a greater volume than the unaffected tin. The expansion produces pustule-like or nodular excrescences at the affected points. Transformation extends radially outward from the spots until the whole mass is infected. The metal then rapidly breaks down to a brittle powder. The disease is infectious and can be propagated by inoculation. Transformation can be begun by contact between a grain of the powder and a piece of sound metal. The metal becomes sick in a manner analogous to that of the human organism when attacked by pathogenic bacteria. Once infected, the whole mass is in danger. Powdery gray tin shows the same analysis as that of the ordinary white metal. In other words, gray tin is an allotropic modification of the elemental metal.

E. Cohen and C. Van Eijk[12] show that the cause of tin pest is the enanthiomorphic change of ordinary white tetragonal tin into gray tin. If white tin be powdered, mixed with some gray tin, and kept at a low temperature, say −50° C., for a few days, the entire mass changes to gray tin; and conversely, gray tin changes to white tin by warming the mass on a water-bath. Measurements of the potential difference of the two forms of tin in a cell with stannous chloride as electrolyte give a zero value at 18° C.; at higher temperature the gray form is the positive pole, and at lower temperatures, the white. The transition temperature is 18° C. Consequently, when the ordinary metal is kept below 18° C.,

[10] *Mem.* Acad. St. Petersburg (1870) (1) **7**, 15.

[11] *Archaeologia* (1899) **56**, 13.

[12] *Versl.* Akad. Amsterdam (1899) **8**, 36, 102. E. Cohen and C. van Eijk: Physikalisch-Chemische Studien am Zinn. *Ztsch. physikal. Chem.* (1899) **30**, 601.

it is metastable, and before equilibrium can occur, it must change into the gray form. White tin under ordinary conditions is in a metastable state; but under ordinary atmospheric conditions, the change is exceedingly slow. The rate of change is accelerated by lowering the temperature, reaching a maximum at about −50° C., and thereafter diminishes as illustrated in Fig. 2. Jänecke[13] observed the change through an extended interval of temperature about 20° C. and 600 atmospheres pressure.

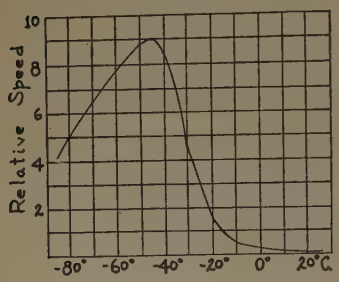

FIG. 2.—RELATIVE SPEEDS OF TRANSFORMATION OF ORDINARY TIN TO GRAY TIN AT VARIOUS TEMPERATURES.

Stepanoff[14] studied the rate of transformation of gray and white tin.

Hasslinger[15] states that a tinned iron vessel showed a crystalline brittle surface after it had been kept at 16° to 45° C. for 2 years. He inoculated other masses of tin with small portions of this crystalline metal. These were transformed in a similar manner, the affected area increasing 3 to 5 mm. in diameter daily. No difference could be noted between experiments at 7°, 19° and 37° C. When tin foil was inoculated, the change extended through the thickness of the foil. The crystalline tin preserves its appearance up to near the melting point, but becomes normal after melting and again solidifying. E. Cohen[16] showed that the structural change of the worked metal consists in a recrystallization process, the result of which is the formation of larger tin crystals from smaller ones; and that the various forms of mechanically worked tin are in a metastable condition with reference to unstrained tetragonal tin above 18° C., and also with reference to gray tin below 18° C.

CHEMICAL CORROSION

Tin is widely used in alloys, in the manufacture of tin foil, and for coating other metals, such as copper and iron, to render them more resistant to corrosion, or for decorative effects. Tin metal itself is very resistant to corrosion by the atmosphere or the various gases contained therein as a result of manufacturing processes. Water affects tin hardly

[13] E. Jänecke: Über einen elektrisch heizbaren Druckapparat zur Untersuchung der Schmelz- und Umwandlungserscheinungen von Salzen, Salzgemischen, Metallen and Legierungen. *Ztsch. physikal. Chem.* (1915) **90**, 257.

[14] *Ann.* Inst. Phys. Chem. Leningrad (1924) **2**, 500.

[15] *Sitzb.* Akad. Wien. (1908) **117**, 501; *Monatsh.* (1908) **29**, 787.

[16] *Chem. Weekbl.* (1905) **2**, 450; (1909) **6**, 625; *Ztsch. Elektrochem.* (1912) **18**, 616; (1913) **19**, 23; *Ztsch. physikal. Chem.* (1900) **33**, 57; (1900) **35**, 588; (1901) **36**, 513; (1904) **48**, 243; (1908) **63**, 625; (1910) **68**, 214. E. Cohen: The Allotropy of Metals. *Trans.* Faraday Soc. (1911) **7**, 122.

at all. At ordinary temperatures there is no tendency toward oxidation. Were it not for the fact that tin is electronegative to iron and strongly accelerates its corrosion in the presence of atmospheric electrolytes if the two metals be exposed at the same time—that is, if the coating be non-continuous—tin would serve admirably as a protection to sheet steel or iron. The corrosion of tin in the form of tin plate in one of its widest uses, that of tin cans, is discussed separately.

Small amounts of tin, when added to other metals or alloys, markedly increase their corrosion resistance. Desch and Whyte,[17] in their studies of the microchemistry of corrosion, show the protective influence of tin on the copper-zinc alloys.

Even the purest water has practically no solvent action on pure tin. Long experience has shown that block tin pipe, when the tin metal of which it is made is of good quality, is one of the best materials for conveying distilled water to be used for experimental purposes. Carbonated water has practically no solvent effect on tin metal. When the solubility of metals in water is determined by the conductivity method, it is found that twice-distilled water has practically no solvent effect on tin when the resultant effect is tested for by delicate conductivity measurements.

It has now been well established that oxygen accelerates and aids the corrosion of tin. Jordis and Rosenhaupt[18] have shown that no oxidation of tin takes place at ordinary temperatures, but that the oxidation does begin at 100° C., taking place only at a slow rate. Below 200° C. tin is oxidized more slowly in moist than in dry oxygen, as a result of the formation of the partially protective coating.

Corrosion by Inorganic Acids

All of the halogen acids attack tin. According to Berthelot, in agreement with the thermal values of the reaction, tin is easily attacked by hydrogen iodide and hydrogen bromide, less readily by hydrogen chloride, and but feebly by hydrogen fluoride. It is slowly dissolved by dilute hydrochloric acid; with hot concentrated hydrochloric acid, hydrogen is evolved and stannous chloride is formed. The dissolution of the tin is accelerated by the presence of a little platinic chloride or if the tin be in contact with copper, silver, lead, platinum, or other of the noble metals. Watts and Whipple[19] found that with normal hydrochloric acid 0.0016 and 0.0015 g. per sq. cm. were dissolved from hammered

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[17] C. H. Desch and S. Whyte: The Micro-chemistry of Corrosion. *Jnl.* Inst. Metals (1913) **10,** 304. See abst. in *Metal Ind.* (1914) **11,** 430; **12,** 115.

[18] E. Jordis and W. Rosenhaupt: Über die Einwirkung von Sauerstoff auf Metalle. *Ztsch. für angew. Chem.* (1908) **21,** 50; *Chem. Ztg.* (1908) **32,** 19.

[19] O. P. Watts and N. D. Whipple: The Corrosion of Metals by Acids. *Trans.* Am. Electrochem. Soc. (1917) **32,** 257.

and cast tin respectively at 38° C. in 20 hr. If potassium permanganate to the extent of about 5 per cent. were present in solution, approximately 0.06 g. per sq. cm. was dissolved from cast tin. The rate of corrosion of cast tin in normal hydrochloric acid is fairly low, and that of hammered tin is about 20 per cent. greater. Since tin dissolves in hydrochloric acid with the evolution of hydrogen, the addition of potassium permanganate, a strong oxidizing agent, rapidly accelerates the corrosion. Hale and Foster[20] found that fifth-normal hydrochloric acid dissolved tin at the rate of 0.42 g. per sq. dcm. per day during 7 days at 20° C., and 0.90 g. during 28 days. The resistance of tin among the metals tested was exceeded only by that of nickel and aluminum, but tin was found to be considerably better than zinc, cast and wrought iron, lead, and copper. The superior corrosion resistance of aluminum was due to the formation of the protective layer of oxide. Whitman and Russell[21] found that the corrosion of tin by hydrochloric acid is increased by the presence of oxygen. Salkowsky[22] states that if hydrogen dioxide be present, free chlorine is evolved and the tin is attacked more readily. Prins[23] found that the presence of easily reducible substances like benzaldehyde or nitrobenzene accelerates the attack of acids on tin. Vaubel[24] states that during the dissolution of polished tin in hydrochloric acid, a black powder is deposited. This dissolves only very slowly, even in concentrated acid. He suggests that this may be a peculiar modification of the metal produced by the reduction of stannous chloride by nascent hydrogen.

Alloys containing tin, antimony, and lead are readily dissolved by a strong solution of hydrochloric acid containing a little nitric acid.

Hot hydrobromic or hydroiodic acid readily dissolves tin. When mixtures of hydrochloric and nitric acids act on tin, ammonia and hydroxylamine are formed.

Chloric acid readily attacks tin, causing it to pass into solution with the formation of stannic chloride, without the evolution of hydrogen and with the production of only very small amounts of stannic acid.

Hypochlorous acid attacks tin, and the action is accelerated by increasing concentrations of the acid, or by the presence of other acids, particularly chloric acid.

Nitric acid readily reacts with tin and exerts a strong corrosive effect. The oxides of nitrogen in small concentrations tarnish tin metal. Nitric acid oxidizes considerably more tin than it dissolves, and hot nitric acid

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[20] A. J. Hale and H. S. Foster: The Action of Dilute Solutions of Acids, Alkalis, and Salts upon Certain Metals. *Jnl.* Soc. Chem. Ind. (1915) **34,** 464.

[21] W. G. Whitman and R. P. Russell: The Acid Corrosion of Metals. *Indust. & Engng. Chem.* (1925) **17,** 348; *München. Med. Wochenschr.* (1925) **72,** 1161.

[22] *Chem. Ztg.* (1916) **40,** 448.

[23] *Proc.* Acad. Amsterdam (1922) **23,** 1449.

[24] *Ber.* (1924) **57B,** 515.

converts the metal completely to hydrated stannic oxide. The products of the action of nitric acid on tin vary greatly with the concentration of the acid and with the temperature. Hale and Foster[25] found that with fifth-normal nitric acid, the loss of metal per sq. dcm. at 20° C. was 4 g. per day in 7 days, and 7.2 g. per day in 28 days. Aluminum and copper are markedly superior in their corrosion resistance to nitric acid. The presence of nitric acid in hydrochloric acid markedly accelerates the corrosion by hydrochloric acid.

The presence of oxygen and oxidizing agents appreciably accelerates the corrosion of tin by nitric acid in various concentrations.

Barth[26] has studied the loss of weight of cobalt-tin, copper-tin-cobalt, and copper-tin-molybdenum alloys in various concentrations of nitric acid.

Tin is appreciably attacked by sulfuric acid, even in dilute solutions. The corrosion is accelerated by the presence of chlorides. In one of the early articles on the corrosion of tin by sulfuric acid, Muir and Robbs[27] studied the effect of the concentration of the acid and the relative proportions of hydrogen, hydrogen sulfide, sulfur dioxide, and sulfur produced. They found that when the molar proportions of sulfuric acid and water are as seven to two at 20° to 25° C., there is but little action. No hydrogen sulfide is produced, but little sulfur, and a trace of sulfur dioxide is formed. At 110° to 120° C. small amounts of hydrogen sulfide and appreciable quantities of sulfur and sulfur dioxide are produced. When the acid and water concentrations are equal at 20° to 25° C., traces of hydrogen sulfide and sulfur are found. At 110° to 120° C. there is a little hydrogen and sulfur, some hydrogen sulfide, and a large quantity of sulfur dioxide. When the acid-water proportions are as one to three, there is only a slow action at 20° to 25° C.; but at 110° to 120° C. much hydrogen sulfide and a trace of sulfur dioxide are formed. When the acid-water concentrations are as one to five, at 25° C. the action is very slow; at 110° to 120° C. hydrogen and a trace of hydrogen sulfide are given off. Watts and Whipple[28] made a careful study of the corrosion of tin in normal sulfuric acid. They found that 0.0006 g. per sq. cm. of tin was dissolved in 20 hr. at 38° C. The addition of sodium chlorate caused an enormous acceleration of the corrosion. With approximately 5 per cent. of sodium chlorate, 0.13 g. of tin per sq. cm. was dissolved in 20 hr. at 38° C. Rather unexpectedly, potassium dichromate was found to reduce the corrosion figure in grams per sq.

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[25] A. J. Hale and H. S. Foster: *Loc. cit.*

[26] O. Barth: Die Erhöhung der chemischen Widerstand-fähigkeit Mechanisch noch gut bearbeitbarer, für Konstruktionszwecke verwendbarer Legierungen. *Metallurgie* (1912) **9**, 261.

[27] M. M. P. Muir: Detection of Tin in Presence of Antimony. *Chem. News* (1882) **45**, 69.

[28] O. P. Watts and N. D. Whipple: *Op. cit.*

cm. from 0.0006 to 0.0003. Instead of strongly accelerating the corrosion, it reduced it to less than half. This effect was the result of the formation of a fine white precipitate which acted as a protective coating. Hale and Foster[29] found that with fifth-normal sulfuric acid at 20° C., 0.022 g. per sq. dcm. per day was lost during 7 days, and 0.25 g. per sq. dcm. per day during 28 days.

Jones[30] states that tin metal stands oleum very well and is useful in making condensing coils where copper would be attacked. The advisability of the use of tin in this connection is questionable, inasmuch as it can be supplanted by cheaper metals which have sufficient corrosion resistance.

Oxygen accelerates the attack of tin by sulfuric acid. In dissolving tin when sulfate electrolytic refining baths are made, it is found that the tin dissolves much more rapidly in the electrolyte if baskets containing the metal be exposed alternately to the solution and to the air. Hydrogen dioxide does not affect the rate of dissolution of tin by sulfuric acid. Pyrosulfuric acid dissolves tin with the evolution of heat, forming stannous sulfate and sulfur oxides. Formaldehyde has little effect in decreasing the corrosion of tin by sulfuric acid.

Van Name and Hill,[31] and Selvig and Enos[32] studied the rate of solution of tin in sulfuric acid and in mine waters containing sulfuric acid and iron and aluminum sulfates.

Pure liquid hydrocyanic acid has no action on pure tin, and probably none on commercial tin. Gray and Hulbirt[33] state that the contact of this acid with commercial tin causes the decomposition of the acid, and that the use of tin in connection with hydrocyanic acid should be avoided. Taplay[34] states that hydrocyanic acid gas plays a part in the corrosion of tinned sheet-iron parts of gas meters employed in connection with the distribution of manufactured gas.

Tin is corroded somewhat by various concentrations of chromic acid. When the acidity is sufficiently high, the determining factor of corrosion is diffusion.

A large number of patents have been taken out for etching agents, employing numerous salts of boric, acetic, tartaric and nitric acids in

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[29] A. J. Hale and H. S. Foster: *Loc. cit.*

[30] G. B. Jones: Materials of Construction Used in a Chemical Works. *Chem. Age* (London) (1921) **4**, 394, 416.

[31] R. G. Van Name and D. U. Hill: On the Rates of Solution of Metals in Ferric Salts and in Chromic Acid. *Am. Jnl. Sci.* (1916) **42**, 301.

[32] W. A. Selvig and G. M. Enos: Corrosion Tests on Metals and Alloys in Acid Mine Waters from Coal Mines. Carnegie Inst. Tech. Coal Min. Invest. *Bull.* (1922) **4**.

[33] California Agricultural Experiment Sta. *Bull.* 308 (1919) 408.

[34] J. G. Taplay: Internal Corrosion of Mains, Services, and Meters. *Gas Jnl.* (1920) **150**, 583; *Gas World* (1920) **72**, 481.

dilute acid solutions for commercial etching. The salts are to be used either singly or in combination with each other. Although these salts themselves do not of themselves readily corrode tin metal, it is probable that they have some influence on the rate of corrosion. The attack of these etching agents is usually more severe along the grain boundaries of the metal surface than in the interior of the grain.

A number of tests to determine the effect of the attack of acetic acid on block tin are reported by Calcott and Whetzel.[35] Their corrosion figures are given in Table 1.

TABLE 1.—*Corrosion of Block Tin by Acetic Acid*
(Calcott and Whetzel)

Acid	Concentration, Per Cent.		Temperature, Deg. C.	Rate of Corrosion, Inches Penetration per Month
Acetic	20		25	0.000412
			B.p.	0.000896
Acetic	60		25	0.000511
			B.p.	0.00131
Acetic	100		25	0.00160
			B.p.	0.0140
	Acid	Anhydride		
Acetic anhydride	10	90	25	0.00169
			B.p.	0.0103
Acetic anhydride	60	40	25	0.00140
			B.p.	0.0456
Acetic anhydride	80	20	25	0.00405
			B.p.	0.0588

Block tin was subjected to the attack of 20, 60, and 100 per cent. acetic acid at 25° C. and at the boiling point of the solutions. Although the data were obtained by one of the early corrosion methods, it clearly indicates that acetic acid may be safely handled in tin, at least up to 60 per cent. concentration. It is very likely possible that at room temperatures somewhat higher concentrations may be stored in tin or tin-lined containers. The results also show that boiling acetic acid should not be handled in tin in concentrations much over 20 per cent.

Whitman and Russell[36] have shown that the corrosion of tin by weak nonoxidizing acids is determined primarily by the oxygen which is dis-

[35] W. S. Calcott and J. C. Whetzel: Laboratory Corrosion Tests. *Trans.* Am. Inst. Chem. Engrs. (1923) **15**, pt. 1, 74.

[36] W. G. Whitman and R. P. Russell: *Loc. cit.*

solved in the liquid. They show also that the presence of hydrogen exerts a retarding influence. The data in Table 2 are taken from their paper.

TABLE 2.—*Corrosion of Tin by Weak Nonoxidizing Acids in Presence of Oxygen and Hydrogen*

Metal	Acid	Concentration, Per Cent. by Weight	Average Penetration per Year			
			Under O_2		Under H_2	
			Cm.	In.	Cm.	In.
Tin.....	H_2SO_4	6	2.20	0.865	0.018	0.007
	HCl	6	5.69	2.24	0.030	0.012
	HNO_3	3	0.325	0.128	0.320	0.126
	$HC_2H_3O_2$	6	1.18	0.465	0.008	0.003

These figures show over a hundredfold increase with sulfuric, hydrochloric and acetic acids in low concentrations when saturated with oxygen. In the case of nitric acid, the effect of dissolved oxygen is not important, because its oxidizing action is overshadowed by that of the acid itself.

CORROSION BY ORGANIC ACIDS

A number of organic fruit acids, such as citric and malic, attack tin quite rapidly in contact with air, but scarcely at all when air is excluded. At any rate, the attack is very much lessened at reduced oxygen pressures. A similar condition holds true for lactic acid, which attacks tin in the presence of oxygen but scarcely at all in vacuo or in an atmosphere of carbon dioxide. Appreciable concentrations of lactic acid definitely corrode tin.

Oxalic and tartaric acids, even in low concentrations, dissolve tin in the presence of air, but the removal of oxygen definitely retards the action.

The presence of pectin substances, particularly in canned tomatoes, materially retards corrosion of tin coatings.

The moist vapors of salicylic acid, according to Whittaker,[37] do not seem to affect tin when the metal is used as a condensing surface. When the vapors of salicylic acid are condensed in iron equipment, they are given a violet coloration; but there is no coloration effect when condensed in tin equipment.

Picric acid shows a definite corrosion effect on tin. Similar to other organic reducible compounds, the acid shows a strong accelerating effect on the corrosion of tin in sodium hydroxide. According to Watts and

[37] H. F. Whittaker: Materials of Construction for Chemical Apparatus. *Trans.* Am. Inst. Chem. Eng. (1923) **15**, 114.

Whipple,[38] amalgamation does not protect the tin, since no hydrogen is evolved.

Phenol tarnishes and corrodes tin. When practically pure phenol is boiled with tin, it becomes opalescent. The phenol vapors are accompanied by benzol, which is a reduction product. This reaction has been studied by Zoller.[39] As a result of the reaction, tin is oxidized. The attack does not seem to take place to any appreciable extent at room temperatures, but only above 100° C.

Jermstad and Gaule[40] found that tin metal was colloidally dissolved from tin tubes when heated for 10 hr. in distilled water or 0.5 per cent. phenol, when the tubes were in rubbing contact. The same concentration of phenol has no effect on tin when pieces of the metal are not in contact. They found that the following solutions, with or without the addition of phenol, had no destructive effect on tin metal: 1 per cent. morphine hydrochloride, 0.01 per cent. atropine sulfate, 0.1 per cent. cocaine hydrochloride, 5 per cent. sodium cacodyl, 0.1 per cent. strychnine nitrate, 25 per cent. caffeine with sodium salicylate, Digalen, 1 per cent. novocaine.

Corrosion by Bases

Tin is readily attacked by sodium and potassium hydroxides. The corrosion in potassium hydroxide has been studied by Nutton and Law[41] with the object of determining the potential of hydrogen liberated from this metal, and the possible application of electrolytic reduction to organic processes. Hale and Foster show that tin is appreciably soluble in caustic soda, giving a weight loss of 0.30 g. per sq. dcm. per day for 7 days, and 0.50 g. per sq. dcm. per day for 28 days. Tin was markedly inferior to all the other metals tested, and was better only than aluminum and lead. Tin corrodes slowly in pure sodium hydroxide solution. Oxidizing agents, such as potassium permanganate or picric acid, markedly intensify the attack. Sodium arsenate and potassium nitrate do not accelerate the corrosion.

In practice, tin is found to dissolve anodically in the tetravalent form, giving stannate as follows:

$$Sn + 4 \oplus = Sn''''$$
$$Sn'''' + 6OH' = SnO_3'' + 3H_2O$$

This, together with the fact that alkaline stannite solutions decompose spontaneously to give metallic tin and stannate, lead to the belief that

[38] O. P. Watts and N. D. Whipple: *Loc. cit.*

[39] H. F. Zoller: The Interaction of Tin and Phenol. *Jnl.* Am. Chem. Soc. (1921) **43**, 211.

[40] *Schweiz. Apoth. Ztg.* (1919) **57**, 89.

[41] Nutton and H. D. Law: The Potential of Hydrogen Liberated from Metallic Surfaces. *Trans.* Faraday Soc. (1907) **3**, 50.

the relation between stannic and stannous ions and tin metal was similar to that between cupric and cuprous ions and metallic copper. Opposed to this was the fact that tin dissolves anodically in acid solutions as stannous ions. Goldschmidt and Eckardt[42] found that although pure tin readily became passive, it also readily dissolved in alkaline solutions to form stannous ions. Foerster and Dolch[43] found that tin metal stannous ion and not tin metal stannic ion is the stable system. Anodic tin readily passivates in alkaline solution as the result of the formation at definite concentrations of colloidal tin compounds which are precipitated on the electrode. This prevents a diffusion of the stannous ions, and the anode potential is raised to the value necessary for oxygen evolution. The oxygen rapidly oxidizes the stannite ion to stannate. Any insoluble impurities present in the tin favor the occurrence of this film action. The higher the temperature and the lower the current density, the more tin can be dissolved before the formation of stannate occurs. Eventually the surface becomes coated with stannic compounds, and the tin becomes passive.

Tin metal is thus seen to be readily corroded by alkalies, but the corrosion may be slowed down as the result of the formation of oxide coatings by the chemical action of the hydroxides on the tin metal.

When present in small amounts in manufactured gas, gaseous ammonia has been considered to cause corrosion of gas mains and the tinned sheet-iron parts of gas meters. Taplay[44] has attributed the corrosion to the products resulting from the reactions between carbon bisulfide and ammonia. Henderson and Galletly[45] state that when tin is heated in ammonia gas, the surface of the metal becomes frosted and blistered. At high temperatures the ammonia is decomposed. The metal seems to "fix" no appreciable amount of nitrogen. If the work of Henderson and Galletly be confirmed, it is probable that the corrosion of gas meters may be due to contact between the ammonia and the iron at imperfections of the tin coating. Liquid ammonia, according to Kraus,[46] does not dissolve tin, but when metallic sodium has been first dissolved in the ammonia, the liquid has a strong solvent action on tin metal. Kraus states that solutions of tin in this reagent are red, and readily conduct the electric current. Hale and Foster,[47] in their corrosion tests on

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[42] H. Goldschmidt and M. Eckardt: Über die Reduktion von Nitrokörpern durch alkalische Zinnoxydullösungen. *Ztsch. physikal. Chem.* (1906) **56**, 385.

[43] F. Foerster and M. Dolch: Über das Verhalten von Zinnanoden in Natronlauge. *Ztsch. für Elektrochem.* (1910) **16**, 599.

[44] J. G. Taplay: *Loc. cit.*

[45] G. G. Henderson and J. C. Galletly: The Behavior of Metals When Heated in Ammonia. *Jnl.* Soc. Chem. Ind. (1908) **27**, 387.

[46] C. A. Kraus: Solutions of Metals in Non-metallic Solvents; General Properties of Solutions of Metals in Liquid Ammonia. *Jnl.* Am. Chem. Soc. (1907) **29**, 1557.

[47] A. J. Hale and H. S. Foster: *Loc. cit.*

tin acted on by ammonium hydroxide, indicate that this reagent is without attack on tin metal.

Tin is readily dissolved and attacked by alkaline pastes which are employed as cosmetics; but it is corroded hardly at all by those materials, such as shaving creams, which are very slightly acid in reaction due to excess of the fatty acids, such as stearic. The use of tin in collapsible tubes for various creams, tooth pastes, and shaving soaps is well known. The average shaving soap is as nearly neutral as possible, and often is found to be slightly acid, due to fatty acids. Lead was found by Beythien[48] to be less susceptible than tin to loss in weight.

Corrosion by Salts

Salt solutions act more rapidly on tin metal than does water. In certain cases, as for example the chlorides, the corrosion is quite marked. Salts which are decidedly alkaline, such as the carbonates and bicarbonates, corrode tin in a manner quite similar to the action of hydroxides.

The halides are among the most active substances corroding tin. The effect of a material known under the name of "Flammon," which consists of a mixture of ammonium fluoride and hydrofluoric acid, on the metals used in the brewing and related industries has been investigated by Will and Landtblom.[49] All percentages of Flammon show no effect on tin metal.

Hale and Foster,[50] in their study of the action of dilute solutions of acids, alkalies and salts upon metals, found that tin is appreciably attacked by calcium chloride solutions of fifth-normal concentrations. Only aluminum and nickel are attacked less, while zinc, cast and wrought iron, lead and copper are more readily attacked. Their results are of the weight-loss type, and at the present time, in view of our much better corrosion methods, are of little value except as indications. The attack on tin was about 1½ times greater than that on nickel, but only about one-third of that on lead.

Solutions of ferric chloride, due to their acidic reaction, markedly affect tin. Together with small amounts of tin chlorides and a little hydrochloric acid, ferric chloride has been patented for the recovery of tin from tin-plated sheets, but to date it has found practically no industrial application.

The attack of tin by magnesium chloride solutions occurs to some extent, but the action is slow, being of the same order as the attack by

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[48] A. Beythien: Metal Tubes for Cosmetics. *Ztsch. Nahr. Genuss.* (1922) **43,** 47. See *Chem. Abstr.* (1922) **16,** 2571.

[49] H. Will and F. O. Landtblom: Effect of Different Disinfecting Agents on Metals. *Ztsch. Ges. Brauw.* (1919) **42,** 81. See *Chem. Abstr.* (1920) **14,** 1176.

[50] A. J. Hale and H. S. Foster: *Loc. cit.*

calcium chloride. The resistance, however, of metals to magnesium chloride, as studied by Hale and Foster,[51] shows that only nickel is superior in its resistance to the attack by this salt. Halla[52] studied the susceptibility of tin plate to attack by neutral magnesium chloride solutions. He found that when the partial pressure of oxygen is high, the corrosion of tin plate in gas meters is accelerated. When, however, the partial pressure of oxygen is lowered by the presence of illuminating gas, the salt seems to retard solution of oxygen in the liquid, and at the same time decreases the corrosion rate.

Hale and Foster[53] state that sodium chloride by itself in fifth-normal concentrations does not corrode tin. The results of other workers, however, seem to indicate that this salt has an appreciable corrosion effect on the metal. Jermstad and Gaule[54] report that when tin test pieces are boiled in a 1 per cent. salt solution and are not in rubbing contact, no tin is dissolved. If the test pieces be in rubbing contact, colloidal solution of the tin takes place. Fink and Mantell[55] have shown that the addition of sodium chloride to dilute solutions of sulfuric acid markedly increase the rate of solution of the tin by the acid. Järvinen[56] studied the attack of tin by sodium chloride solution.

When an outside electromotive force is impressed on a cell in which tin is the anode in a sodium chloride solution, the metal dissolves at a relatively slow rate.

Stannous chloride readily attacks tin metal. It has often been suggested in connection with acids and other salts as a detinning material for the removal of tin from tin-plate scrap. It accelerates corrosion of tin by mineral acids. Stannous chloride attacks the metal most readily at the grain boundaries. It has been used as an etching reagent in the microscopic study of tin and its alloys.

Salt solutions, such as warm aqueous solutions of ammonium chloride, potassium hydrosulfate, potassium aluminum sulfate, and many other soluble sulfates and chlorides dissolve tin; but solutions of sodium nitrate, potassium nitrate, sodium tetraborate and sodium hydrosulfate have relatively little action.

The action of 10 per cent. ammonium persulfate in sulfuric acid solution causes marked corrosion. Ammonium sulfate, ammonium sulfocyanide, and ammonium thiosulfate all corrode tin. The action of cal-

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[51] A. J. Hale and H. S. Foster: *Loc. cit.*

[52] F. Halla: Über das Rosten von Weissblech in Magnesiumchloridlösungen. *Jnl.* Gasbeleuchtung (1913) **56**, 908; *Chem. Zentr.* (1913) **2**, 1709.

[53] A. J. Hale and H. S. Foster: *Loc. cit.*

[54] *Schweiz. Apoth. Ztg.* (1919) **57**, 89, 109.

[55] C. G. Fink and C. L. Mantell: Reduction Roasting, Leaching, and Electrolytic Treatment of Bolivian Tin Concentrates. *Eng. & Min. Jnl.* (1928) **125**, 452.

[56] *Ztsch. Untersuch. Nahr. Genuss.* (1925) **50**, 221.

cium hypochlorite on tin is somewhat analogous to the action of hypochlorous acid. White[57] states that when calcium hypochlorite is in contact with tin, oxygen is liberated, and that the hypochlorite slowly oxidizes tin to stannic oxide with the evolution of chlorine. There are a number of references in the literature concerning the action of alkali hypochlorites on tin. They all agree that there is appreciable destruction on the metal surface. Weston[58] has investigated the effect of small amounts of calcium hypochlorite in water upon tin and other metals. In dilute solutions, the action is relatively slow.

Taplay,[59] as a result of his investigation of the corrosive effect of ferric sulfocyanide on tinned sheet-iron parts of gas meters, has come to the conclusion that this salt has little corrosive effect.

Potassium chlorate and sodium chlorate markedly accelerate the solution of tin and tin alloys when they are subjected to attack by mineral acids. Watts and Whipple[60] have shown that the accelerating effect of these salts is several hundredfold in normal sulfuric acid solution. Eckelmann[61] employed sodium chlorate in a rapid analytical method for the solution of alloys of tin in concentrated hydrochloric acid with the addition of a small amount of concentrated nitric acid.

Halla[62] finds that potassium cyanide hinders the corrosion of tin plate.

It might be expected that potassium dichromate or sodium dichromate, being strong oxidizing agents, would greatly accelerate the corrosion of tin in nonoxidizing mineral acids. As the result of the formation of an insoluble coating on the metal, the tin is protected from further destruction, and potassium and sodium dichromate are thus found to have passivating action instead of accelerating corrosion.

Van Name and Hill[63] found, as a result of their study of the solution of tin in potassium ferric sulfate and sulfuric acid, that when the acidity of the solution was sufficiently high, diffusion became the most important factor in the velocity of the corrosion.

Potassium ferricyanide is generally believed to be without corrosive attack on tin. It has been used in the conventional Walker or ferroxyl test[64] for the detection of pinholes in tin coatings, especially tin plate.

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[57] A. D. White: Action of Solutions of Bleaching Powder and of Hypochlorous Acid on Metals. *Jnl.* Soc. Chem. Ind. (1903) **22,** 132.

[58] R. S. Weston: The Corrosive Action of Water on Metals. *Jnl.* New Eng. Water Works Assoc. (1910) **24,** 559.

[59] J. G. Taplay: The Corrosion of Dry Gas Meters. *Gas World* (1918) **69,** 230; *Gas Jnl.* (1918) **144,** 359.

[60] O. P. Watts and N. D. Whipple: *Loc. cit.*

[61] *Chem. Analyst* (1918) **25,** 22.

[62] F. Halla: *Loc. cit.*

[63] R. G. Van Name and D. U. Hill. *Loc. cit.*

[64] W. H. Walker: The Detection of Pin Holes in Tin Plate. *Ind. & Eng. Chem.* (1909) **1,** 295.

The reagent consists of a mixture of 50 parts gelatin, 450 parts water, 1 part potassium ferricyanide, and 1 part sulfuric acid. When spread over a tin-coated surface and allowed to set, blue spots appear at the pinholes. This reagent allows us to detect pinholes so small as not to be readily observable by the naked eye.

Burns[65] states that a simple and convenient method for finding pinholes in tin coatings on steel consists in immersing the plated part for about 4 hr. in a dilute salt solution containing a trace of hydrogen peroxide. The solution is made by adding 5.8 g. of sodium chloride and 3 c.c. of 3.6 per cent. hydrogen peroxide to a liter of water. The pinholes are revealed by the development of spots of red iron rust. The larger pinholes appear within 30 min., the smaller ones after 1 or 2 hr. Thus it is possible to get an idea of the size of the pinholes by observing the rate of appearance of the rust spots.

Pitschner[66] states that the American Chain Co. at Bridgeport, Conn., has developed a very satisfactory modification of the Walker test which consists in the application of the ferricyanide reagent to paper with the ingredients in different concentrations. The paper is wetted and applied to the clean surface, taken off in about 2 min., and examined for blue spots which are indicative of the porosity of the coating.

Potassium and sodium nitrates, in spite of the fact that they are strong oxidizing agents, do not accelerate the solution of tin in alkalies. Potassium nitrate itself exerts only a slow corrosion effect.

Acid solutions of potassium permanganate are reduced by tin and cause solution of the metal with roughening of the tin surface. The tin is oxidized and the permanganate reduced. In their study of the influence of oxidizing agents on the corrosion of metals, Watts and Whipple[67] show that the presence of a small amount of potassium permanganate in a normal hydrochloric acid solution accelerates the corrosion rate almost 40 times, while in normal sodium hydroxide the corrosion is only 20 times greater.

Sodium acetate affects tin only at a slow rate.

Jermstad and Gaule[68] have reported that a 0.35 per cent. solution of sodium acid arsenate affects tin with the production of a noncolloidal solution of the metal. The normal sodium arsenate, despite the fact that it is an oxidizing agent, shows no accelerating effect on the corrosion of tin in sodium hydroxide, although its own solutions cause appreciable tarnish on tin plate.

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[65] C. T. Thomas and W. Blum: Protective Value of Nickel Plating. *Trans.* Am. Electrochem. Soc. (1927) **52**. See discussion by R. M. Burns, p. 284.

[66] C. T. Thomas and W. Blum: *Op. cit.* See discussion by K. Pitschner, p. 283.

[67] O. P. Watts and N. D. Whipple: *Loc. cit.*

[68] *Schweiz. Apoth. Ztg.* (1919) **57**, 89, 109.

Whittaker[69] finds that tin is a satisfactory material of construction to resist solutions of sodium hydrosulfite. The best materials of construction to insure cleanliness of the product are tin, nickel and monel metal. They not only withstand corrosion by solutions and suspensions of the salt itself, but also the other reagents that are met with in the process of manufacture. This does not include the first step of the process—that is, digestion.

Corrosion by the Halogens and Sulfur

The halides in their free form unite directly with tin, forming stannic salts. Fluorine does not react readily with tin at low temperatures, but at 100° C. it forms stannic fluoride. Dried chlorine and bromine act on tin at ordinary temperatures. Liquid chlorine markedly attacks tin. Even in low concentrations, when mixed with other gases, the free halogens markedly attack the metal. Tin is readily susceptible to attack by iodine, whether in the form of solution or vapor. The rate of solution of tin is abnormally high, as shown by the work of Van Name and Bosworth[70] in their study of the attack of various metals by a solution of iodine in potassium iodide. Iodine vapors, even in low concentrations, rapidly tarnish tin metal and tin coatings. Tammann[71] showed that tin was soon colored yellow when placed in a desiccator in an atmosphere of iodine vapor, and that a fine, dark dust gathered on the surface of the metal.

As early as 1850, Wohler[72] studied the action of sulfur chloride on tin. He found that the reaction took place readily and to a marked degree. His results agree with those of Nicolardot,[73] who found that of all the metals only tin, aluminum, mercury and iron react with sulfur chloride. In 1916, Domanicki,[74] after reviewing all previous work on this reaction, found that ether accelerates the combination as a result of the formation of a complex between the ether and the sulfur chloride.

Thionyl chloride reacts with most of the common metals and metalloids. North and Hageman[75] state that when tin is heated in a sealed

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[69] H. F. Whittaker: *Op. cit.*

[70] R. G. Van Name and R. S. Bosworth: On the Rates of Solution of Certain Metals in Dissolved Iodine, and Their Relation to the Diffusion Theory. *Am. Jnl. Sci.* (1911) **32,** 207.

[71] G. Tammann: Über Anlauffarben von Metallen. *Ztsch. anorg. Chem.* (1920) **111,** 78.

[72] *Liebig's Annalen* (1850) **73,** 375.

[73] P. Nicolardot: Action du protochlorure de Soufre sur les Metalloides et sur les Metaux. *Compt. rend.* (1908) **147,** 1304.

[74] N. Domanicki: Reaction of Sulfur Chloride with Metals. Catalytic Action of Ether. (Abstr. from *Jnl.* Russian Phys. Chem. Soc. (1916) **48,** 1724. Chem. Soc. *Jnl. Abstr.* (1917) **112,** 369.

[75] H. C. North and A. M. Hageman: The Action of Thionyl Chloride on Metals and Metalloids. *Jnl.* Am. Chem. Soc. (1912) **34,** 890.

tube with thionyl chloride to 150° to 200° C., reaction takes place with the formation of stannous chloride, sulfur dioxide and sulfur chloride. In the presence of an excess of thionyl chloride, the stannous salt is oxidized to the stannic form. At lower temperatures, thionyl chloride has an appreciable action on tin metal.

The affinity of tin for sulfur is not very great, although the two elements unite when heated. The reaction is vigorous and usually accompanied by incandescence. Schütz[76] lists the affinity for sulfur of seven metals in the following order: manganese, copper, nickel, iron, tin, zinc, and lead. Hydrogen sulfide, even in dilute concentrations, tarnishes tin metal. The discoloration in tin cans has been shown by Mantell and Lincoln[77] to be due to sulfides of tin. When moist, sulfur dioxide is markedly destructive of the surface of tin metal, forming some stannous sulfide but also oxidizing the tin to metastannic acid.

Corrosion by Organic Compounds

The resistance of tin metal to attack by organic compounds is quite varied. The effect on the metal of various organic acids has been discussed. The reactions of tin with the hydrocarbons, both saturated and unsaturated, have been little studied except in the case of acetylene. This gas, when either pure and dry or impure and moist, does not perceptibly attack tin metal. Acetylene gas in a pure dry state was passed over tin by Reckleben and Scheiber[78] for 20 min. without any deleterious effect. The recommendation has been made that tin be applied as a protective coating to apparatus or metal surfaces which come in continuous contact with acetylene gas. Hodgkinson[79] found that tin was unaffected by acetylene at high temperatures.

When in contact with tin metal, carbon bisulfide, particularly when impure, readily tarnishes polished tin surfaces. Beyond a tarnishing effect, the attack is relatively little.

Many of the nonferrous metals react with chlorinated hydrocarbons. Berger[80] describes reactions between tin and carbon tetrachloride, hexachlorethane, hexachlorbenzol, chloroform, tetrachlorethane, and hexachlorcyclohexane. These, as well as other chlorinated and haloge-

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[76] E. Schütz: Über die Affinität des Schwefels zu einer Reihe von Metallen. *Metallurgie* (1907) **4,** 659.

[77] C. L. Mantell and E. S. Lincoln: Corrosion of Tin in Tin Cans. *Can. Chem. & Met.* (1927) **11,** 29.

[78] H. Reckleben and J. Scheiber: Wirkt Acetylen auf Metalle ein? *Chem. Ztg.* (1915) **39,** 42.

[79] W. R. Hodgkinson: Some Reactions of Acetylene. *Jnl.* Soc. Chem. Ind. (1918) **37,** 86-T.

[80] E. Berger: Production de chlorures par réactions amorcées. *Compt. rend.* (1920) **171,** 29.

nated hydrocarbons corrode tin metal. In many cases the action is accelerated by free acid they may contain, free chlorine, or decomposition products formed by their exposure to sunlight and heat.

Formaldehyde, when in contact with tin metal, causes no noticeable effect, but when it is oxidized to formic acid it corrodes tin. It is known that when as little as 1 per cent. of formaldehyde is present in solutions of the common mineral acids, their attack on steel is markedly lessened, but the same effect does not hold true in respect to tin metal.

Pyridine and pyridine bases have been stated at various times to be partially responsible for the corrosion of tinned parts in gas meters and gas lines, although this statement is disputed by some investigators. The same holds true for cyanogen and cyanogen compounds.

The action of photographic solutions on tin has been studied by Crabtree, Hartt and Mathews.[81] They find that tin and alloys containing tin tend to produce high initial fog when the metal is used as a container for photographic developers. This fog later decreases to a normal value when the solution acquires better developing powers. There is a definite indication of the possibility of the use of a tin alloy or metallic couple which will gradually discharge tin into the developer and act as a preservative of the solution. If the tin be in contact with another metal, the fog it creates in the developed plates is materially increased. Tin as a metal is one of the least suitable for use as a material of construction for photographic apparatus such as trays, tanks, clamps and pipes for conveying photographic developers and fixing solutions. Practically all the other nonferrous metals are more suitable. In the case of developer tanks, tinned or tin-lined brass faucets should be carefully avoided. Tin, solder, or any alloy containing tin should be eliminated from all developing apparatus.

Schönfeld[82] and Hirt[83] attribute the turbidity resulting in beer which has been in contact with tin to the presence of acids contained in the beer or originally in the wort. The turbidity is said to be approximately proportional to the acidity, which may be removed by treatment with neutralizing agents such as limestone or calcium carbonate. Neutralized beer is without attack on tin and is immune to tin turbidity.

Drugs, such as caffeine even up to 20 per cent. solution, or caffeine containing small amounts of sodium salicylate, have no solvent action on tin either at ordinary or at elevated temperatures up to the boiling point.

The widespread use of tinned apparatus in the production, transportation and preparation of milk leads one to the belief that the metal has

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[81] J. T. Crabtree, H. A. Hartt and G. E. Mathews: Effect of Electrolysis on the Rate of Corrosion of Metals in Photographic Solutions. *Ind. & Eng. Chem.* (1924) **16,** 13, 81.

[82] F. Schönfeld: Metalltrübungen in Bieren. *Chem. Ztg.* (1910) **34,** 1144.

[83] *Wochschr. Braueri* (1910) **27,** 633.

been found by experience to be exceedingly satisfactory for this work. Milk has practically no corrosive effect on tin metal, irrespective of the length of time during which it is exposed, or the temperature. Sour milk readily corrodes tin in tin plate, due to the lactic acid formed. Much of the corrosion found in cream separator parts which are made of stamped sheet steel coated with tin has been found to be due to lactic acid formed by the souring of the milk left in the separator as the result of careless or insufficient cleaning.

Sugar solutions, particularly in canned foods, serve to protect tin from corrosion by vegetable acids, according to Lehmann[84] and Carles.[85] More recent work by the National Canners' Association does not confirm this in all respects.

Tin metal is slightly soluble in its fused salts, particularly when these are subjected to electrolysis. If the temperature of the melt be allowed to drop rapidly, the fused salt fogs as a result of the metal precipitating out of the solution in the form of minute drops, which give the melt a dark color.

Corrosion of Tin Plate by Food Products

The problem of corrosion of tin cans by food products which are packed, stored, or canned in these containers is complicated by the large number of factors entering into the situation. Tin cans are made of tin plate. It is understood that it is an exceedingly difficult matter to form a perfectly continuous coating of tin over the iron base metal.

It is commonly conceded that when tin plate is exposed to atmospheric influence, corrosion takes place most rapidly at those points where iron is exposed. Small electrolytic cells are set up, and the corrosion of the iron plate is actually accelerated by the presence of the tin. When in contact with an electrolyte, iron and tin will function as a battery, iron being the anode and tin the cathode. The tendency will, therefore, be for the iron either to oxidize or to disintegrate, and for corrosion to be accelerated. Corrosion can proceed so far as actually to cause holes to form in the tin plate at those points at which there is uncovered iron.

Corrosion of tin-plate containers used for food products produces at least three different types of results: first, that which is known as discoloration, which results in tarnishing, darkening, or blackening the bright metal surface of the inside of the container; second, termed perforation, which results in the formation of holes in the cans to the detriment and spoilage of the enclosed food products (it will be shown that perforation is the result of electrolytic action); and third, that which we will term solution, the result of chemical action of the food-product

[84] *Arch. Hyg.* (1907) **63**, 67.
[85] *Bull. Agr. Intelligence* (1919) **10**, 621.

constituents on the metal of the container. The resulting action does not usually produce discoloration, but makes itself evident in other ways. One of the most usual is termed "etching" which is descriptive of the effect. It is not meant by this classification that these factors are entirely separate and do not occur together, but it will be shown that they may occur separately without relation to each other, if conditions are favorable; or that they may supplement each other or occur progressively.

Discoloration is largely the result of chemical action of the food-product constituents, or resulting products of these, on the metals of the container. If any electrolytic action does occur, it is of secondary importance.

It is well known that many food products, such as the legumes (corn, peas, beans, etc.), contain sulfoproteins. These materials, as a result of the processing of the foods in canning, may break down and produce hydrogen sulfide or related compounds. Iron is affected by hydrogen sulfide, with the resultant formation of black iron sulfide. Tin is also affected by hydrogen sulfide, with the resulting formation of black or brownish black stannous sulfide. With small amount of sulfides, the effect of the attack on tin may only be evident as a tarnish whose color may vary from blue to brownish black. The iron sulfide would be more readily formed, the iron being attacked more readily than the tin.

In the case of food products, it is easy to observe the formation of "can black" on the covers of tin containers. Where iron has been exposed, the black iron sulfide forms readily. The attack on tin is less rapid. Chemical analysis confirms the statement that can black is iron sulfide. The tarnish on tin where iron has not been exposed is stannous sulfide. This has been confirmed both by microscopic examination, duplication of similar tarnishes on pure tin by the action of dilute hydrogen sulfide solution, and by chemical analysis. Duplication was done on both electrolytic tin and commercial tin sheet. The samples were matched microscopically. There is no doubt that to a large extent discoloration is due to sulfide formation.

In some of the large number of cans examined, there was a tarnish which was not stannous sulfide but looked like stannous oxide. Other sections of the can showed some iron sulfide tarnish in an adherent layer, usually along the intercrystalline boundary. In this connection, the action of organic acids on tin is of interest. In the absence of air, tin is not oxidized by such acids as tartaric, but, in the presence of air, oxidation of the metal takes place at the surface of the solution, the oxides of tin and stannous tartrate being formed. With a restricted amount of oxygen, the corrosion product first formed is stannous oxide. This stannous oxide may be gradually oxidized further with the production of a brown colloidal material. This substance on heating may be converted to the bluish white hydrated stannic oxide. Dilute oxalic,

tartaric, citric, malic, acetic and lactic acids all attack the tin coatings of cans rapidly in the air, at a slower rate in the presence of restricted amounts of air, but scarcely at all in vacuum or in an atmosphere of carbon dioxide. All of the acids oxidize more than their equivalent of tin, the main product being stannous oxide or stannous hydroxide. It is fairly adherent to the surface of the metal.

If a pair of electrodes, one of iron and the other of tin metal, be immersed in the contents of a tin can containing food products preserved in saline solutions, an e.m.f. will be generated. The potential is very small and is only indicated on a sensitive millivoltmeter. The remarkable happening is that the voltage will rise to a peak value, fade off, drop to zero, and then build up to a peak value in the reverse direction. Mantell and Lincoln[86] observed that the phenomenon of reversal of potential occurs only with those foods preserved in strong electrolytes. The term "strong electrolytes" is used from the viewpoint of the theory of electrolytic dissociation. The fact that potentials are reversed is indicative that the iron has been passivated, and instead of being, as usual, less noble than tin, it becomes more noble than tin. Instead of functioning in an electrolyte as anode, its position is changed to that of cathode. The manner of passivation of the iron is relatively unimportant. It might be caused by a gaseous film, or a thin oxide layer, formed as a result of electrolytic action, or even as a result of chemical action. Examples of foods which show the phenomenon of reversed potentials are corn, peas, and beans. These do not have perforation effects, but all cause discoloration when canned.

In contradistinction to those food products which are put up in strong electrolytes, most fruits, berries, etc., are put up in sugar solutions. These weak electrolytes are of low conductivity and high resistance, while the saline solutions are of high conductivity and low resistance. There is ordinarily no reversal as shown on a millivoltmeter with iron and tin electrodes. As a general rule, those foods which do not show a reversal of potential do not give discoloration troubles, but do give perforation difficulties. If there be no reversal of potential, the iron has not been passivated, and at exposed spots the iron will be the anode, tin the cathode, and both in contact with the electrolyte. Galvanic action will be set up and the anodic iron disintegrate, which if carried far enough will cause perforation of the can.

Kohman and Sanborn[87] conducted experiments to determine the mechanism of the corrosion of tin and iron, both when in contact and when not in contact, in fruits, and the relation of the results to the electrochemical theory of corrosion. They found that in a number of fruits

[86] C. L. Mantell and E. S. Lincoln: *Loc. cit.*

[87] E. F. Kohman and N. H. Sanborn: Tin Plate and the Electrochemical Series. *Ind. & Eng. Chem.* (1928) **20**, 76.

tin is anodic to iron. Although not all fruits were studied, the data indicate that this is a rather general condition in canned fruits. Many of the facts which did not conform to the older idea that tin is cathodic to iron are readily explained in accordance with these new findings. They likewise made electrical measurements which bear out the results of the corrosion tests that tin is anodic to iron. The nature of corrosion in fruits is distinctly different from that in solutions of the fruit acids. The results are in harmony with commercial experience.

For the sake of clarity at this point it is assumed that none of the constituents of the food products in the can can chemically dissolve tin. This condition may not exist as such in any actual specific food product. In order to avoid electrolytic action and resultant perforation, it would be necessary to have only one metal exposed to the action of the contents of the can. If there be two dissimilar metals, there will be electrolytic corrosion. In the case of tin cans, the only manner by which we can obtain the condition that only one metal be exposed to the action of the electrolyte, is to have the steel surface of the base metal completely covered by tin metal.

The work of Kohman in his studies on perforation in the case of Bing cherries, strawberries and loganberries, shows that oxygen accelerates corrosion; but with the removal of the oxygen, perforation is not prevented. Excessive extension of the exhaust with resultant air removal does not prevent perforation. The basic explanation for perforation can be seen to be electrolytic. Kohman offers the explanation for the lack of hydrogen production in cans of those fruits which develop holes, as being due to depolarizers or oxidizing agents which convert the hydrogen to water.

It is not the usual condition that there is no chemical action on the tin of the tin plate by the contents of the can. It is quite usual to have chemical action on the tin by organic acids along with or preceding electrolytic action. The corrosion of tin by organic acids has been extensively studied by workers who were experimenting without reference to the canning industry. Citric, a common fruit acid, definitely etches tin, the attack being most pronounced along the intercrystalline boundaries. The tin crystals on the surface of tin plate are elongated, flattened and distorted due to the mechanical working, polishing and cleaning that the tin plate receives in its manufacture and fabrication. Malic acid, occurring in apples, readily attacks tin in the presence of air. With lessened amounts of air the attack will not proceed as rapidly. Acetic acid attacks tin and its alloys. While particularly evident in sour milk, lactic acid is also found in other foods.

With the exception of canned clams, all canned foods show pH values lower than 7; that is, they are acid in reaction. While the effects of the different foods show slight variations, the general results are the same.

The etching due to peaches is somewhat small, but the detinning action of spinach is quite severe. The chemical attack of the acids in spinach on the tin of tin cans has been reported a number of times in the German and American literature. The action of pumpkin and squash is quite the same as that of spinach. The constituents of rhubarb, grapefruit and apples markedly attack tin plate. It would be expected from what is known of the effects of vegetable acids that the detinning action of cider and berries would be severe in a relative sense. This is found to be the case.

Perforation troubles are usually associated with those food products containing constituents which chemically attack tin. If we were to have a completely tinned sheet free from pinholes and exposed iron, in contact with those foods, we would not expect electrolytic action at first but we would expect chemical attack. If the chemical action be continued long enough, enough tin will eventually dissolve to expose the iron of the base metal. When this happens, we will again have two metals in contact with the electrolyte, with the iron as anode and the tin as cathode. If there be no neutralizing factors—that is, if the attacking constituent be neither consumed nor brought to equilibrium—no matter how heavy a coating of tin is put on tin cans, perforation will eventually occur.

Let us return to the subject of discoloration. This has been shown to be largely due to the action of sulfides and sulfocompounds. Iron and tin sulfides are both black, an objectionable color in food products. Many metals form white sulfides, an example of which is zinc. It is thought that before the advent of the so-called "sanitary" can, the use of zinc chloride flux for soldering the cans effectively prevented discoloration. Paper liners in the cans of food products which discolor badly have been effectively used, the paper containing zinc salts.

Enameled or lacquered cans have been used, the additional coating being made on tin plate. It is no less difficult to make a perfectly continuous coating of enamel or lacquer on a commercial scale on tin plate than it is to make a perfectly continuous coating of tin on the base steel plate. Chemical attack on the tin is usual in the case of those foods which perforate. If the enameled or lacquered coating on the tin plate be not perfectly continuous, chemical action of the constituents of the food product, instead of being spread over the whole area of the can, will be localized at those points where the coating is not continuous and the tin plate is exposed. With localized action, corrosion will be accelerated and perforation will result more rapidly than in an unenameled can. Commercial experience has shown that enameled cans perforate more readily than those which are not enameled.

There seems to be a definite field for containers in which tin is absent; that is, a container made of sheet iron with an enameled surface. If the enameled coating on the steel plate were not continuous, the exposed iron

would be chemically attacked and rusted. The commercial feasibility of making such a container with a minimum of uncovered iron spots is an open question. How much rusting would occur in cans made of enameled sheet steel or how objectionable this rusting would be is not known. A large number of tinless cans have been used for fish products. The cans stood up very well. The food products were preserved in better condition than in ordinary cans.

There has been one major improvement in containers, namely, the development of what is known in the industry as the "C-Enamel Lined Can." This C-Enamel was developed primarily to prevent iron sulfide discoloration in canned corn, and for this purpose it has been eminently successful. It has also been found that C-Enamel will prevent iron sulfide discoloration with clams, lobster, shrimp and crabmeat.

C-Enamel is made by specially baking plate, under very accurate heat control, that has been coated with a lacquer composed of oil and gums that have been specially treated and mixed with an exceedingly small amount of zinc oxide. The small amount of zinc oxide present is completely imbedded and protected in the enamel, so that practically none of it comes out into the canned food. The total amount in the enamel is so small that even if it all came out in the food, the Bureau of Chemistry's tolerance for zinc in foods would never be reached. This C-Enamel is designed only for nonacid foods, and cannot be used with acid foods, as acid will disintegrate the enamel. The regular enamel used with acid foods is of entirely different character. G. S. Bohart of the National Canners' Association Laboratories showed the efficacy of a minute amount of zinc oxide in a coating medium. A patent was taken out in his name and made available to the industry. Commercial can makers have developed C-Enamel on the basis of his discovery.

Although much of the foregoing would seem to justify the conclusion that the tin can leaves much to be desired as a perfect container for preserving foods, it is well to remember that there is not available at the present time as good a substitute which has all the commercial features of the tin can. Glass containers would eliminate corrosion, but they are not suitable or adaptable for cheap shipping and transportation. Paper containers will not ordinarily stand processing of foods. Metal containers other than those made of tin plate bring along their own corrosion problems. They are also more costly. Tin cans are relatively cheap because of the quantities in which they are made and consumed.

Commercially, it is to be observed that even with its defects the tin can is adapted to a great many different food products. Food-product losses due to can failures bulk very large in actual money, although the percentage of cans failing is low. An estimate of the size of the industry can be gained from the fact that approximately 8,000,000,000 cans per year are used in the United States.

A factor to be considered in tin cans and their use is the thought that in many cases the use of tin in cans is decorative. At other times it is, or should be, protective.

H. A. Baker of the American Can Co. summarizes the status of the tin can in the canned-foods industries. He states that for foods such as peas, the tin can is practically a perfect container. It is very satisfactory for tomato pulp and paste, asparagus, tomato and other soups, baked beans, red beans, string beans, lima beans; and very little difficulty is experienced with succotash. The tin can has served admirably as a container for spaghetti, pears, peaches, apricots, pineapple, prunes, grapes, raisins and figs, as well as ripe olives.

Tin cans give no trouble when oysters are canned in them. In the case of sardines, no trouble is attributable to the use of the tin can. While formerly no sealing compound was used in the curl of sardine can covers, at the present time practically all sardine cans are sealed with a lining compound so that hermetic closing is possible and oil seepage prevented.

Such trouble as has been experienced with canned milk Baker states is not attributable to tin plate.

In the case of tomatoes, there are no difficulties when this food is properly prepared, closed and cooked. Formerly very considerable difficulty was experienced in the case of corn from discoloration. The use of C-Enamel cans over a period of years shows that this trouble can be completely eliminated. Apparently it is only a question of time when no corn will be packed in containers other than the C-Enamel can. Sweet potatoes, as a result of improper preparation, cause discoloration. Hominy often discolors the inside of tin cans. Unless special methods are used, a great deal of trouble with discoloration is found when okra is packed in tin cans.

Clams formerly caused considerable difficulty due to discoloration. The use of paper liners as well as C-Enamel cans almost entirely eliminates this trouble. Tin cans are excellently adapted for the packing of salmon, although slight discoloration accompanies this use of tin plate. With improved canning methods now in use, the packing of tuna fish in tin cans is very satisfactory. In the case of lobster, the discolorations formerly caused by this product have been eliminated almost entirely by the use of paper liners or C-Enamel cans. The tin can is satisfactory for the wet-pack method of preserving shrimp. The C-Enamel can prevents all formation of iron sulfide in the wet pack. In the dry pack, iron sulfide formation is also practically controlled, although with this dry product there may be at times slight signs of iron sulfide formation, as the enamel is not so efficient when liquid is not present. The C-Enamel can will not prevent the formation of a certain amount of rust with dry-pack shrimp, but this can be prevented by sealing the can in vacuum. Paper liners containing zinc salts have been very successfully

applied to shrimp, lobsters and other sea foods, particularly among Canadian and Japanese packers of these products.

It is recommended that heavy grades of tin coatings be used in the case of canned meat. Baker states that much of the trouble which has been experienced is not attributable to the tin plate used for the containers.

It is generally believed that the tin can is an ideal container for sauerkraut, despite the fact that we might expect lactic acid corrosion. The detinning action of spinach is very severe. It is a hard product to hold in a tin can, and special preparation of this food is necessary when it is to be canned. The tin can is not satisfactory over long periods for the preservation of grapefruit. Special canning methods are necessary for canning the product to preserve it even for short periods. It is difficult to preserve the flavor of grapefruit in tin cans. Pumpkin and squash have a severe dissolving action on the tin coating. The contents of the can are affected. Enameled cans, however, are highly satisfactory. Apples have often caused considerable trouble from perforations when they are stored or preserved in tin cans. Some of the difficulty is attributable to the method of preparation of the product.

It is interesting to note that very little difficulty is encountered in canning white cherries; but black cherries are probably the most severely perforating article ever packed in tin cans. Red sour cherries cause much trouble from perforation, some of which is attributable to improper preparation. It is recommended that charcoal plate (a heavier grade of tin plate) be used. An enamel coating is necessary to preserve the color of the cherries. Heavy tin coatings should be used for apple butter, although the container is at best only a temporary one. The same difficulties as are found with red cherries occur with plums. Baker states that tin plate itself gives no trouble when syrup is canned, but that considerable difficulty is experienced because of improper preparation.

Enameled cans must be used for beets because of the bleaching action of the tin, and the destruction of the color of the beets. In the case of rhubarb, the tin can is very unsatisfactory except for a short period of preservation. Very little difficulty is found with jams and preserves. The ordinary tin can is not a satisfactory container for strawberries or blueberries. The chance of perforation is very high. Enameled cans of charcoal plate should be used for strawberries to preserve the color, while the same is not necessary for blueberries. Enameled cans must be used to preserve the color in huckleberries, but the chance of perforation is very great. Cranberries in tin cans should be regarded at best only as a semiperishable article. Black raspberries give fairly good results if not kept too long. Red raspberries and loganberries can with reasonable safety be preserved in tin cans, although as a result of the bleaching action of the tin, enameled cans must be used to preserve the

color. Tin cans are readily perforated when employed for canning cider. They are an unsatisfactory container for this product.

Corrosion of Tin Alloys

It is interesting to note some of the high points in the corrosion of some of the simple binary tin alloys.

When too much tin is alloyed with aluminum, the resulting metals are brittle and easily oxidized. A 15 per cent. tin 85 per cent. aluminum alloy falls to powder after a few days. Richards[88] described a strong malleable alloy with 10 per cent. aluminum, which, after standing a few months, lost all its malleability. It became as rotten as dried clay. Annealing did not restore its strength. If the alloy be fabricated into sheet and portions of the sheet heated, small globules sprout in all directions. These have the same composition as the alloy. Alloys with 15 to 50 per cent. aluminum are attacked by water at ordinary temperatures with the evolution of hydrogen.

The hard tin-arsenic alloys give rise to arsine, AsH_3, when treated with hydrochloric and other nonoxidizing mineral acids, while alloys with an excess of arsenic are not attacked by hydrochloric acid.

The tin-barium alloys are readily corroded by atmospheric influences. With appreciable percentages of barium, they are decomposed by water, leaving a tin skeleton.

In connection with corrosion of alloys by mercury, it is interesting to note that an alloy of two parts tin and one part cadmium, cut into chips on a milling machine about 0.05 mm. thick, 12 mm. long, 1 to 3 mm. wide, and closely packed, without jamming, into a tube 1 cm. in diameter, 50 cm. long, was found by Welo[89] to be an effective bar to the passage of mercury vapor from a mercury high-vacuum pump to the vessel to be exhausted. This was shown by means of spectrograms taken after allowing the pump to stand connected to the exhausted vessel through the tube containing the alloy.

Similar to the tin-barium alloys, the tin-cadmium metals are rapidly attacked by water, air, and dilute acids.

The alloys of tin and cerium tarnish rapidly, even when polished and covered with oil. They are very unstable against corroding influences. All the alloys containing less than 80 per cent. tin are pyrophoric. The alloys above 50 per cent. cerium produce showers of sparks when merely scratched with a hard object. The Ce_2Sn compound has the maximum hardness, about 6 on the von Moh scale. It is very unstable in air, and vigorously reacts with water.

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[88] J. W. Richards: Aluminum, 338. H. Carey Baird, Philadelphia, 1890.

[89] L. A. Welo: The Absorption of Mercury Vapor by Tin-cadmium Alloy. *Phys. Rev.* (1917) Ser. 2, **10**, 583.

In the tin-copper alloy series only one compound, Cu_3Sn, is shown on the equilibrium diagram. It appears as bluish gray or bluish white lamellae. It is rapidly attacked by hot concentrated hydrochloric acid.

Merica[90] tells of the corrosion of a copper roof which had been coated with tin as an added protection. The corrosion was not attributed to solubility of tin in water but to the action of water as an electrolyte in contact with the pure tin and a series of tin alloys directly underneath.

Some white tin-copper alloys, usually approximating Cu_4Sn, admit of a brilliant polish. Many of these alloys show considerable resistance to tarnishing. They were formerly used for mirrors and hence were called speculum metals. They are sometimes used in the construction of mirrors for optical instruments. Their composition ranges from 30 to 34 per cent. tin and 62 to 69 per cent. copper. In some cases lead, zinc, arsenic, silver, nickel, or antimony has been added. The typical alloy is 70:30. The term art bronzes is applied to alloys which are employed for statuary, vases and ornaments of all kinds. A considerable number of these alloys owe their corrosion resistance to the formation of protective corrosion coatings. In a number of statues the proportion of copper ranges from 72 to 91 per cent., tin 0.15 to 10.2 per cent., zinc 0.1 to 26 per cent., lead up to 3 per cent., and small proportions of iron, nickel and antimony.

The tin-copper alloys are remarkably resistant to ordinary atmospheric corrosion. Their use for statuary, either in binary, ternary, or quaternary systems, is well known. Many of the coveted honors in life are perpetuated in bronze. An example is the Victoria Cross, the highest military decoration of the British Empire. These were struck from gun metal taken from the trophies of the previous wars.

Many bronzes have resisted the corrosion of ages, having been recovered from graves, bogs, beds of lakes and rivers, buried cities, and from the earth. The corrosion crusts of these are generally termed patina, of which there are several kinds: malachite, $CuCO_3.Cu(OH)_2$; atacamite, $CuCl_2.3Cu(OH)_2$; and azurite, $2CuCO_3.Cu(OH)_2$, admixed with silver, stannic oxide, iron oxide, and cupric and lead chlorides. These patina are the result of surface attacks by waters which contain oxygen, carbon monoxide, and a greater or less percentage of salts. The soluble salts that are formed are removed by solution, while the bronzes become covered according to circumstances with an insoluble layer of either the carbonate or the oxide whereby the form of the objects is preserved.

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[90] P. D. Merica: Structure of the Coating on Tinned Sheet Copper in Relation to a Specific Case of Corrosion. U. S. Bur. Stds. *Tech. Paper* No. 90 (1917). For abstract see *Trans.* Am. Inst. Metals (1916) **10,** 109; *Metal Ind.* (London) (1916) **9,** 618. See also *Met. & Chem. Eng.* (1916) **15,** 415, and (1917) **16,** 657.

Fink and Eldridge[91] have devoted considerable study to the restoration of antique bronzes. Metal corrosion is very strongly evidenced in the ancient bronzes found in our public or private museums. Scientists have constantly endeavored, with questionable success, to restore articles so attacked to their original condition. Variation in the composition of bronzes is undoubtedly responsible for the lack of a scientific method for cleaning. A method which may be successful in restoring one bronze may have no satisfactory effect on another of like composition.

There are two classes of bronze corrosion: the green crust which coats bronze and other copper alloys that have lain buried in the ground, and the bronze disease, akin to the familiar tin pest. The red, green, or brown layers on ancient bronzes are composed chiefly of copper, lead and tin minerals in the article which have been attacked by the nitrates and nitrides of the soil in which they have lain, forming a crust of copper oxychlorides and oxycarbonates, and tin oxide. A layer of copper oxide lies beneath this crust, often covering a core of metal. Sometimes the entire mass of bronze is converted to these compounds, leaving none of the original metal in the specimen. Moisture of the ground, whether clear water or water containing dissolved salts, is another important corroding agent. There are some evidences that former methods of removing corrosion crust were drastic. Some samples show without doubt that strong chemicals such as mineral acids had been applied. Others carry the marks of a chisel, denoting the use of crude mechanical means. Fink and Eldridge,[92] in their work along these lines, found that the details of design in the original bronze were exactly reproduced in the layer of copper oxide which lies beneath the outer crust. Their fundamental idea was to replace cathodically the metal that had gone into the crust, since corrosion is generally conceded to be an electrolytic reaction. Experiments determined that the use of a 2 per cent. solution of caustic soda as electrolyte was the safest for this purpose. The corroded object, without any preliminary cleaning, is hung in this bath as cathode, totally immersed. If the specimen be particularly soft as a result of attack, it is often necessary to wind it in several coils of fine annealed copper wire, or pack it in white sand. Anodes of iron, duriron, or platinum are hung on either side of the article. The container is generally a glass jar, although large tanks of heavy sheet iron or stoneware may be used, depending on the size of the bronze. Low current densities are preferred. The evolution of hydrogen at the cathode will alter the crust to a powdered or spongy copper. When the gas is freely given off, the object is removed from the bath and washed by soaking several times in warm water. The film of reduced copper is brushed from the specimen,

[91] C. G. Fink and C. H. Eldridge: First Report on the Restoration of Ancient Bronzes and Other Alloys. Metropolitan Museum of Art, New York, 1925.

[92] C. G. Fink and C. H. Eldridge: *Loc. cit.*

provided the latter were of hard metal under the corrosion crust, or is taken off by means of an acid dip if no core of metal be present. The exposed oxide surface, smooth and metallic, preserves all details of design.

Some gun metals have shown remarkable corrosion resistance, as is exemplified by the Swedish guns with the inscriptions 1535 and 1632 which were recently salvaged from the sea. The bronze had suffered very little corrosion action, although it had been submerged nearly 300 years.

The bronzes are attacked by the free halides. Alloys with at least 50 atomic percentage of tin are most resistant to the action of hydrochloric acid mixed with ferric chloride, while the alloy corresponding to 80 per cent. atomic weight of copper has the greatest resistance to hydrochloric acid alone. Sulfuric acid attacks bronze much less vigorously than either copper or tin. Ammonia dissolves copper from bronze containing 1 to 12 per cent. tin, but is almost without action on bronze with 25 per cent. tin. Nitric acid acts less vigorously on bronze than on copper. Certain of the bronzes become passive and resistant to corrosion as the result of the formation of a film of stannic oxide.

The tin-gold alloys corresponding to the compositions Sn_2Au and SnAu are strongly resistant to attack by the mineral acids. The alloy corresponding to the composition Sn_4Au is attacked by nitric acid and colored brown as a result, while the alloy approximating the composition Sn_2Au is resistant to the action of nitric acid. The tin-gold alloys have at times found use as cheaper substitutes for the more expensive noble metal applications for resistance to corrosion and chemical attack. Infrequently tin-gold alloys have been used in jewelry and for decorative work.

In connection with the tin-iron alloys, a method for determining the amount of alloyed tin in tin coatings has been devised by Kohman.[93] The unalloyed tin readily dissolves in a hot solution of sodium plumbite, while the iron-tin alloy does not dissolve nearly as readily. The percentage of alloy in a tin coating on ordinary coke plates is readily increased by keeping the steel sheet immersed in molten tin and allowing it to come to the temperature of the tin bath prior to passage through the tinning machine. Kohman found that in ordinary commercial charcoal plate, the alloyed tin constituted about 5 per cent. of the weight of the coating, while in commercial coke plate the amount of alloyed tin was about 17.5 per cent.

Rawdon[94] states that the effect of the alloyed tin upon the service behavior of the coated iron with respect to corrosion is of no practical importance, inasmuch as the compounds of tin and iron bear the same

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[93] E. F. Kohman and N. H. Sanborn: The Tin-iron Alloy in Tin Plate. *Ind. & Eng. Chem.* (1927) **19**, 514.

[94] H. S. Rawdon: Protective Metallic Coatings. Chem. Catalog Co., New York, 1928.

general electrochemical relation toward iron that tin does. He further states that the alloy formation does not increase the corrosion resistance, since the alloys, like tin, afford no electrochemical protection to iron against corrosion attack. He believes that since the alloy layer is always extremely thin, the possibility of the mechanical properties of the coating being adversely affected is a very remote one.

In tin smelting, the tin-iron alloys are known as hardheads. These show considerable resistance to attack by the mineral acids, the organic acids, and the alkalies. They are obtained in a more or less pure condition in smelting operations, in the crucibles or the forehearths, or on the beds of furnaces. They form a pale to dark gray, irregularly granular or crystalline, brittle, more or less completely fused mass. Hardhead generally consists of more or less metallic tin mechanically intermingled with the alloys of definite composition which appear to be chemical compounds.

An interesting application of corrosion resistance to tarnishing by tin-lead alloys is in Fahlum brilliants used for stage jewelry. This is a 40 tin 60 lead alloy, which when molten is cast into molds, facetted like cut diamonds. The finished brilliants showily reflect the light from their bright white surfaces.

Rawdon[95] related an instance of corrosion of tin-lead alloy boiler safety plugs which were subjected to moist heat for a considerable period of time. The tin had been changed to an infusible oxide and probably this corrosion was due more to the presence of oxygen in the steam than to the steam itself.

The tin alloy pewter is a comparatively durable alloy if properly handled. It tarnishes on exposure to air, but this tarnish or patina does not detract from the value of the specimen. Corrosion does not readily attack pewter, nor is the alloy subject to "season cracking," a disintegration brought about through hardening. It may be cleaned with a composition of soap and kieselguhr, applied by means of a polishing bob. The ancient methods employed sand and often elm leaves or plants. These contained siliceous matter. Unless cleaning materials are completely removed from the joints of pewter objects, there is a tendency to loosen these connections.

Analogous to the alkaline earth metals, the tin-lithium alloys are readily corroded. They react with water, the lithium being attacked to leave a tin skeleton. They are all white and silvery in color. They oxidize readily and are attacked by most chemical reagents.

Of the tin-magnesium alloys, Phipson[96] claimed that the alloy with 85 per cent. tin 15 per cent. magnesium was lavendar blue. It decom-

[95] H. S. Rawdon: Some Types of Non-ferrous Corrosion. *Trans.* Am. Electrochem. Soc. (1921) **39**, 227.

[96] T. L. Phipson: On Magnesium. *Proc.* Roy. Soc. (1864) **13**, 217.

posed water at ordinary temperatures. Beck[97] states that the molten alloy containing 50 per cent. tin absorbs 40 per cent. of nitrogen.

The tin-mercury alloys have been largely used in the past for silvering mirrors. When alloyed with a third metal in ternary systems, they have been and are employed in dentistry. The tin-mercury alloys are not ordinarily resistant to sulfur tarnishing, nor are they as satisfactory for use in the manufacture of mirrors as is silver metal.

Tin is ordinarily thought of as a deleterious constituent to platinum, inasmuch as the tin-platinum alloys are less resistant to corrosion in many cases than is platinum itself. This is particularly true in the case of resistance to fused salts.

The tin-potassium alloys are similar as far as corrosion is concerned to the alkaline earth metals. Gay Lussac and Thénard[98] found that a mixture of seven volumes of tin filings to two volumes of potassium united with slight incandescence. A fusible brittle alloy was formed. The material had a fine-grained structure, oxidized quickly in air, and decomposed water. When larger proportions of potassium were employed, the alloy took fire when heated in air. A number of investigators have found that the tin-potassium alloys are pyrophoric and liberate hydrogen from water. It is interesting to note that the tin-potassium alloys rapidly attack glass and even steel when they are molten.

The tin-silver alloys are employed in making dental amalgams. Many of them are particularly resistant to corrosion and tarnishing by foods and the digestive fluids of the human oral cavity. The binary alloy appears to undergo profound changes through the lapse of time. Black[99] showed that fresh filings of tin-silver alloys require 50 per cent. more mercury for amalgamation than do similar filings which have been aged for several months or heated to 100° C. for a half hour. The aging does not occur in a bar of alloy during several weeks' heating under the same conditions where filings are aged in an hour. Exclusion of air does not affect the results.

The tin-sodium alloys, analogous to the tin-potassium series, are readily attacked by water, atmospheric influences, acids, and alkalies. The compound $NaSn_2$ is the softest and toughest of all. This material, as well as NaSn, looks the same as tin metal. Mathewson[100] states that a freshly cut surface of the Na_4Sn or the Na_2Sn alloy soon becomes covered in the air with a bronze film. When protected by oil, the surface

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[97] E. Beck: Studien über die Darstellung von Legierungen nitridbildender Metalle. *Metallurgie* (1908) **5**, 504.

[98] *Metall und Erz* (1816) **1**, 40.

[99] A Work on Operative Dentistry, **2**, 309. Chicago, 1914; *Dental Cosmos* (1895) **37**, 353, 469, 553, 571, 637, 737; (1896) **38**, 43, 965, 982.

[100] C. H. Mathewson: Über die Verbindungen von Natrium mit Zinn. *Ztsch. anorg. Chem.* (1905) **46**, 94.

of the Na_2Sn compound resembles that of tin, while the color of the Na_4Sn material is steel blue. The Na_4Sn_3 compound shows a pale blue color on a freshly cut surface.

The tin-strontium alloys are similar, as far as corrosion resistance is concerned, to the tin-barium alloys. They are difficult to prepare as a result of the rapid oxidation of the strontium metal under ordinary atmospheric influences. Even with protective layers of fluxes, considerable metal is lost. With appreciable percentages of strontium, they are decomposed by water, leaving a tin skeleton.

A summary of the applications of tin in industry as a material to resist corrosion shows its marked utility in connection with the preparation of distilled water where the metal is the preferred material of construction; in apparatus in which food products are made, stored, or preserved, such as tinned kettles and tin cans; in the collection, transportation, and distribution of milk; and in the manufacture and use particularly of the tin-copper alloys, such as the sea-water bronzes, the gun metals, and phosphor bronze. Phosphor bronze resists the corrosion of sea water better than copper, and mine waters better than iron and steel. Many of the so-called hydraulic or high-pressure bronzes are markedly resistant to the corrosion action of steam and condenser water. The use of Admiralty metal and copper-tin alloys to resist severe corrosion is well known.

DISCUSSION

W. S. Smith, Carteret, N. J.—Does Dr. Mantell know whether sodium silicate has any inhibiting effect on the action of dilute caustic on tin, similar to its effect mentioned in another paper on aluminum?

C. L. Mantell.—Sodium silicate, from preliminary work, has been shown to have an inhibiting effect.

W. S. Smith.—Then, just in the interest of accuracy, for of course, a few errors are bound to slip into a great mass of data of this sort, on page 128, there is the statement: "Potassium and sodium nitrates, in spite of the fact that they are strong oxidizing agents, do not accelerate the solution of tin in alkalies. Potassium nitrate itself exerts only a slow corrosion effect."

That is not true, because one of the main detinning processes, which was in use for a great many years, depended on the very fact that nitrates accelerate the solution of tin.

U. R. Evans, Cambridge, England.—This paper will be extremely serviceable to all those who have to deal with tin and tin plate. There are just two points which I would like to mention.

Tammann's estimate of the time needed to form the first visible layer of oxide coating on tin metal in dry air is quoted as being 36×10^8 years. Needless to say, I have not personally verified that figure, but Tammann's estimates of thickness are based upon an optical assumption which I fear is inexact. He assumed that it is possible to measure the thickness of a coating by dividing the thickness of the air

film needed to give the same color by the refractive index of the material. That assumption, in my opinion, is based on a wrong optical idea. I reached this conclusion some years ago on theoretical grounds. Quite recently one of my research students, Mr. Bannister, has been investigating experimentally the assumption, which is the basis of Tammann's method of estimating thicknesses, and he finds that the method introduces a considerable error. I fear that the figure quoted will probably have to be modified, if we live long enough to see the first visible layer appear on tin.

Coming to the reversal of polarity between tin and iron, which is an important matter in connection with the deterioration of tin cans, Dr. Mantell did a very great service in calling attention to this reversal. It occurs, as a matter of fact, with many metals other than tin or iron; I have been able to verify the reversal in quite a number of pairs of metals.

However, I find it rather difficult to accept in an unmodified form, Dr. Mantell's interpretation of the reversal, because chlorides would tend rather to militate against the passivity of the iron. I have been interested in the recent work done in the United States by Lueck and Blair; their theory is extremely interesting and probably explains a great many of the phenomena. If I understand it right, they assume that if tin and iron are in contact (as in an imperfectly coated tin can), and if the conditions are such that the main corrosion is of the hydrogen-evolution type, hydrogen escapes most easily from the iron which has the lowest over-potential, and the current will therefore flow in such a direction as to make the iron the cathode and tin the anode. This is most likely to occur in the presence of acids. If the corrosion is of the oxygen-absorption type (as in nearly neutral solutions containing plenty of oxygen or oxidizing agents) other effects will come in, and quite often the iron will be the anode. This principle seems to explain a number of the effects noticed.

E. S. Lincoln, New York, N. Y. (written discussion).—Dr. Mantell's work was prompted by the investigation made for the canning industry by the writer in 1923, and his continuation of these studies has proved the advisability and correctness of the original investigation, which has been of material assistance to the canner.

The canners have been confronted with a tremendous economic loss, due to the perforation and discoloration of cans. One result of this investigation was to show the packers the value of using enamel as an additional protective coating to prevent discoloration in certain food products. In the past, canners had been educated to the use of the term "corn black," indicating that the corn alone was responsible for this discoloration. The proper term, as Dr. Mantell has brought out, is, of course, "can black," as this discoloration is due to imperfections in the can.

When I first discovered the reversal of potential between tin and iron, as referred to in this paper, I used a comparatively low-resistance millivoltmeter, together with an iron and tin electrode inserted in the contents of a can of corn. Later on in the investigation, I realized the desirability of a high-resistance millivoltmeter, and when the same tests were repeated, the action was not so rapid. The following figures illustrate this:

Millivoltmeter 19.5 Ohms Resistance		Millivoltmeter 19.5 Ohms Resistance	
Millivolts	Seconds to Reverse	Millivolts	Seconds to Reverse
2	2	30	4

In these measurements, all conditions remained the same except the resistance of the millivoltmeter.

Furthermore, reversal takes place, regardless of whether or not an electric current is passed between the tin and iron electrodes.

What currents actually pass in the can itself are, of course, not known, and the many variables would greatly affect the amount which, in any event, would be extremely small.

C. L. Mantell.—It is gratifying that some of our early work on tin plate and tin can corrosion has been the subject of so much interest, and has been followed by the excellent and detailed work of such men as E. F. Kohman and N. H. Sanborn of the National Canners' Research Laboratory, and Messrs. Lueck and Blair of the American Can Co., as well as a number of others whose work has thrown more light on the subject with greater understanding of it.

Some New Developments in Acid-resistant Alloys

By Burnham E. Field,* New York, N. Y.

(New York Meeting, February, 1929)

The chemical industry is constantly looking for new materials which either are more resistant to corrosion than those now available or have improved physical properties to meet the requirements of higher temperatures and greater pressures. Attack by acids is one of the more important forms of corrosion and in the last few years the development of acid-resistant alloys has been quite rapid. Perhaps the most notable example is that of nitric acid, the problem of which has largely been solved by the chromium-iron and chromium-iron-nickel alloys. Sulfuric acid may be handled in lead, iron, or the iron-silicon alloys, depending on conditions. As to hydrochloric acid, no metal or alloy can be called entirely satisfactory for handling this acid under plant conditions.[1]

The results of our investigations on the resistance of the nickel-molybdenum alloys to hydrochloric acid have been confirmed by those of Guertler, Rohn, Schulz, Jenge, and others,[2] but thus far only one such alloy has approached commercial production in Germany; this contains approximately 15 per cent. chromium and 7 per cent. molybdenum with the remainder chiefly nickel. Dr. S. W. Parr, as far back as 1914, developed a complex alloy known as "illium," with a nickel base and containing some molybdenum.[3] Dr. Parr was primarily interested in an alloy for lining bomb calorimeters, and while illium does show good resistance to acid it is too expensive for general use. Two United States

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* Union Carbide and Carbon Research Laboratories, Inc.

[1] S. Schein: Storing, Distributing and Using HCl Acid in the Plant. *Chem. & Met. Eng.* (1928) **35,** 673.

[2] W. Guertler: Molybdän als Legierungsbestandteil. *Ztsch. f. Metallkunde* (1923) **15,** 151, 251.

W. Guertler: Das Problem der Säuerfesten Metallischen Werkstoffe. *Ztsch. f. Metallkunde* (1926) **18,** 365.

W. Guertler und T. Liepus: Chemisch Beständigkeit einer Anzahl Metalle und Legierungen besonders mit Molybdängehalten. *Ztsch. f. Metallkunde* (1925) **17,** 310.

W. Rohn: Säuerfeste Legierungen mit Nickel als Basis. *Ztsch. f. Metallkunde* (1926) **18,** 387.

E. H. Schultz und W. Jenge: Chemisch Beständige Legierungen und Ihre Eigenschaften. *Ztsch. f. Metallkunde* (1926) **18,** 377.

W. Rohn: Säuerfeste Metalle und Legierungen. *Korr. und Met.* (1928) **4,** 49.

[3] S. W. Parr: Development of an Acid-resisting Alloy. *Trans.* Amer. Inst. Metals (1915) **8,** 211. U. S. Patent No. 1,115,239.

patents[4] have been granted to Alvah W. Clement, relating to alloys of nickel, molybdenum, and iron, in which the iron content was specifically limited to a maximum of 10 per cent. One of them also limited molybdenum to 10 per cent. while the other specified a maximum of 40 per cent. molybdenum.

The work of which this paper describes a part was started several years ago because certain rather complex nickel alloys showed what was considered an unusual resistance to corrosion. This developed into a fairly general investigation first of binary and then of ternary nickel alloys in an effort to find some that would be chemically resistant and

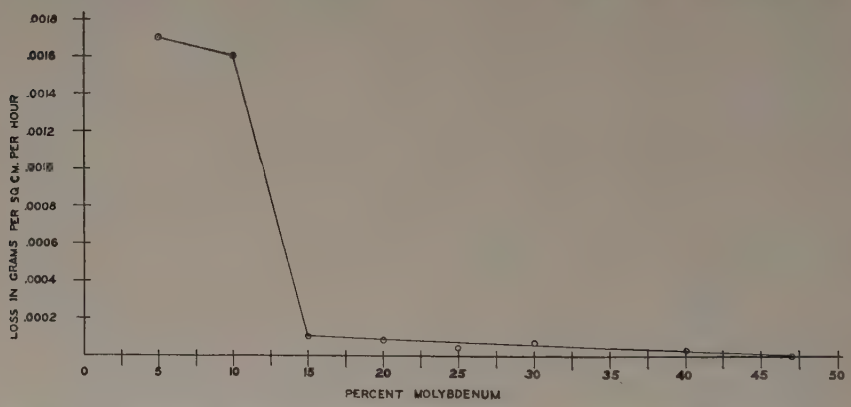

FIG. 1.—CORROSION OF NICKEL-MOLYBDENUM ALLOYS IN 10 PER CENT. HCl AT 70° C.

also have physical properties qualifying them for commercial use. The nickel-molybdenum alloys having been discovered to possess resistance to hydrochloric acid, a fairly complete series of these alloys containing molybdenum up to the eutectic 49 per cent. was studied. Fig. 1 gives the corrosion curve for binary nickel-molybdenum alloys in 10 per cent. hydrochloric acid at 70° C., with molybdenum varying from 5 to 47 per cent. While the alloys with more than 15 per cent. molybdenum are satisfactory from a corrosion standpoint, they have the disadvantage of being rather expensive, and further investigation was made to determine to what extent iron might be substituted to reduce their cost and improve their workability.

It had been believed that not over 10 per cent. of iron could be introduced without adversely affecting the acid resistance, but this investigation developed the interesting fact that maxima occurred in the corrosion curves at from 5 to 10 per cent. of iron. Beyond these maximum points the curves dipped again but with a second rise beyond 25 per cent. of iron. Fig. 2 shows the corrosion curves in 10 per cent. hydrochloric acid and 10 per cent. sulfuric acid for alloys containing 20 per cent. molybdenum and iron varying from zero to 40 per cent.

[4] A. W. Clement: U. S. Patents Nos. 1375082, 1375083.

Curves of similar nature were obtained for alloys containing 15 and 25 per cent. molybdenum with iron varying over the same range. The curves bring out the fact that corrosion does not become rapid until iron reaches 25 per cent. or more. Additional determinations of cor-

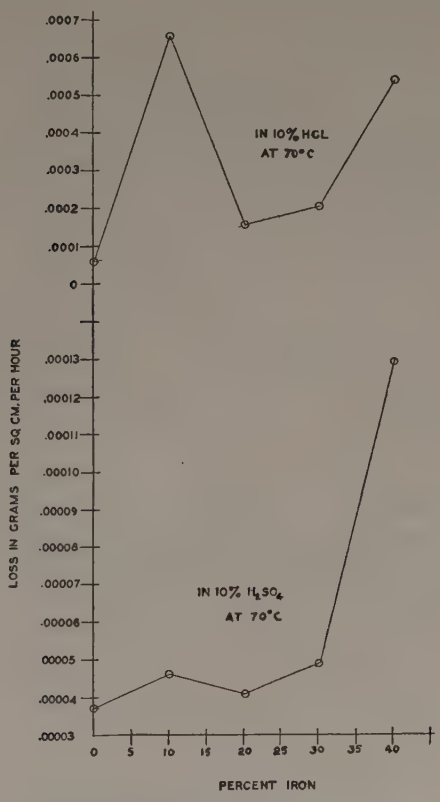

FIG. 2.—CORROSION LOSS OF NICKEL-MOLYBDENUM-IRON ALLOYS. 20 PER CENT. MOLYBDENUM, 0–40 PER CENT. IRON.

rosion as related to iron content were made later, after the effects of other elements in the composition had been studied, when the same general form of curve was obtained. The curve in Fig. 3, corrosion related to iron content in 10 per cent. sulfuric acid, shows that the rate of corrosion between 15 and 25 per cent. iron changes very slowly. The curve shown in Fig. 3 was made on alloys that contained carbon, manganese, vanadium and silicon in the amounts given on page 152, whereas the alloys used in determining the curve shown in Fig. 2 did not contain manganese and vanadium, and contained only small amounts of carbon and silicon.

The selection of the final proportions of molybdenum and iron was an effort to compromise corrosion resistance, cost, and workability of the alloys. Figs. 2 and 3 show that an iron content as high as 20 per cent. with molybdenum also at 20 per cent. would be safe as to corrosion.

With more than 20 per cent. molybdenum it would not be possible to increase the iron appreciably and the cost would therefore rise out of proportion to the gain in corrosion resistance. With molybdenum above 20 per cent. the alloys become stiffer and more difficult to forge. The curves of the three most important factors, corrosion, cost, and workability, seemed to intersect at 20 per cent. molybdenum and 20 per cent. iron with the remainder chiefly nickel.

The effect of other elements has been studied, since it is not feasible to make an alloy absolutely free from impurities on a commercial scale. The effect of increasing carbon is to harden and stiffen the alloy and at the same time decrease its resistance to acid. The best results are obtained

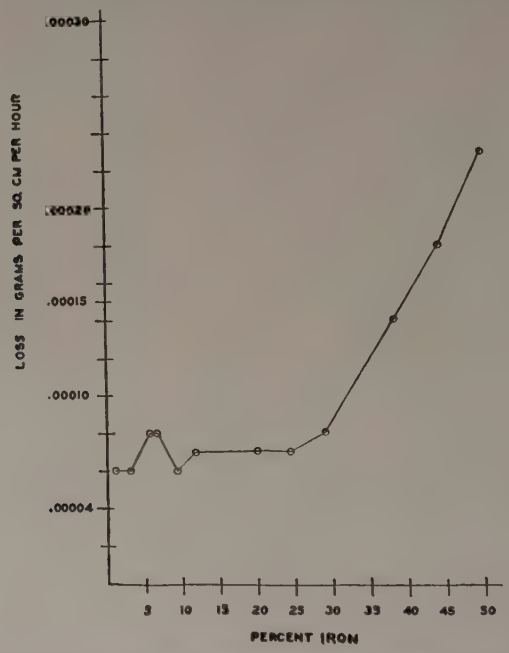

FIG. 3.—CORROSION OF NICKEL-MOLYBDENUM-IRON ALLOYS IN 10 PER CENT. H_2SO_4 AT 70° C.

with carbon not over 0.2 per cent. and it is not difficult to meet this specification commercially. Manganese, as in other nickel alloys, improves the workability and until more than 3 per cent. manganese is added no detrimental effect on the acid resistance is noted. In small amounts silicon has little effect but more than 0.5 per cent. affects the workability adversely. Vanadium in small quantities is valuable as a scavenger and a small amount of residual vanadium has been found to improve the acid resistance. Magnesium is useful in counteracting the detrimental effect of sulfur that may be present in the raw materials.

The nickel-molybdenum-iron alloy is resistant to cold acids, except nitric, showing as little as 0.000001 g. lost per sq. cm. per hr., or 0.00003

in. penetration per month in 37 per cent. HCl at room temperature. Tests of 20 to 24 hr. duration under fully aerated conditions have also shown high resistance towards hot acids, at 70° C. and at the boiling points. In hydrochloric acid of 10 to 37 per cent. strength, the loss at 70° ranges from 0.00005 to 0.00008 g. per sq. cm. per hr., the stronger acid being the less corrosive; at the boiling point, corrosion is about 10 times faster. This corresponds to a penetration of about 0.002 in. per month at 70°. In sulfuric acid of 10 to 77 per cent. strength, the loss at 70° falls from 0.00007 g. in the weaker to 0.00003 g. per sq. cm. per hr. in the stronger acid; at this temperature, corrosion in 25 per cent. sulfuric acid is no more rapid than in that of 77 per cent. strength. At boiling point, the stronger acid is the more corrosive. In formic acid at 70°, the loss averages 0.00008 g. per sq. cm. per hr. over the range from 10 to 85 per cent. strength.

Oxidizing agents such as chlorine attack the alloy with considerable rapidity and it is not recommended for use with chlorine unless the gas is dry. Solutions containing mixtures of acid and oxidizing salts also attack the alloy more rapidly than acid alone. It stands up well in a salt spray,

FIG. 4.—OXYACETYLENE WELD IN NICKEL-MOLYBDENUM-IRON SHEET. PHOTOMACROGRAPH. × 3.

is practically unattacked by alkalies, and shows fair resistance to hydrogen sulfide in acid solutions, and to sulfurous acid.

When tested in comparison with certain well-known commercial alloys in acids at 70° C., the nickel-molybdenum-iron composition shows practically the same resistance towards 10 per cent. sulfuric acid as the best of these, while in 10 per cent. hydrochloric acid its resistance varies from 10 times that of the most resistant other alloy to 18 times that of another well-known composition. In general, it is easier to develop resistance towards sulfuric than towards hydrochloric acid, but the nickel-molybdenum-iron alloy appears about equally resistant to either acid at 10 per cent. strength and at 70° C.

The more important physical properties of the alloy are given in Table 1, which shows that the alloy in the worked state has physical properties which compare favorably with those of many high-grade steels. It is readily machinable; it can be hot-rolled into sheet and still further cold-rolled if a finer surface is desired. Cold work hardens the alloy but

it can be softened again by a short anneal at approximately 1050° C. Excellent castings can be made in sand. Welding with the oxyacetylene torch presents no particular difficulty to an experienced welder but the use of a flux is recommended to prevent oxidation, which would be detrimental to the acid resistance. Fig. 4 is a photomacrograph of an oxyacetylene weld made in nickel-molybdenum-iron sheet with rod of the same material. Sections cut from experimental welds similar to this have shown practically the same resistance to hydrochloric acid as the unwelded sheet; this is an unusual circumstance and is particularly advantageous for the fabrication of acid-resistant equipment.

TABLE 1.—*Physical Properties of Nickel-molybdenum-iron Alloy*

Specific gravity, forged	8.8
Weight per cu. in., lb	0.315
Weight per cu. ft., lb	514
Melting point	1300° C.
Coefficient of expansion, in. per ° C	10.7×10^{-6}
Thermal conductivity per ° C., cal. per sq. cm. per cm. per sec	0.004
Electrical resistivity, microhms per cm. cube at 24° C	126.7
Electrical conductivity, per cent. that of copper at 24° C. (75° F.)	1.4
Shrinkage, sand castings, in. per ft	¼
Forgings: yield point, lb. per sq. in	51,700–69,100
ultimate strength, lb. per sq. in	112,600–117,300
elongation in 2 in., per cent	33.5–24.1
reduction in area, per cent	37.9–31.2
Brinell hardness, average	207
Rockwell B. hardness, average	97
Erichsen test: hot-rolled sheet	5.0
annealed sheet	8.0

Figs. 5 to 8 give a good idea of the character of the structure of the nickel-molybdenum-iron alloy. Fig. 5 is a photomicrograph of the alloy cast in an ordinary ingot mold; the structure of sand-cast metal is similar except that it is a little coarser, due to slower cooling. Fig. 6 shows the structure of the same metal after the ingot has been forged to a bar 1 in. square. The darkly etched constituent in Fig. 5 has been broken up and in Fig. 6 appears to be a eutectic. Fig. 7 is the same as Fig. 6 and shows that of the two constituents of the eutectic one is a solid solution and the other is probably a ternary compound of nickel, molybdenum, and iron. Fig. 8 shows the structure of hot-rolled sheet which has been reheated to 1050° C. As the reheating temperature is raised, the particles of compound appear to be partly absorbed by the solid solution.

Another acid-resistant alloy has been developed which shows some promise for commercial work; it is a nickel-base alloy but contains no molybdenum. Nickel-silicon alloys with up to 10 per cent. of silicon are fairly strong but not particularly acid resistant; at about 15 per cent. silicon they become resistant to acid, but very brittle. Approximately

the same applies to nickel-aluminum alloys except that the zone of brittleness and resistance to acid is a little higher, being in the vicinity of 20 per cent. aluminum. Of the ternary nickel alloys in this group, the only one that combines useful strength with fairly good acid resistance is the one containing approximately 10 per cent. silicon and 5 per cent. aluminum.

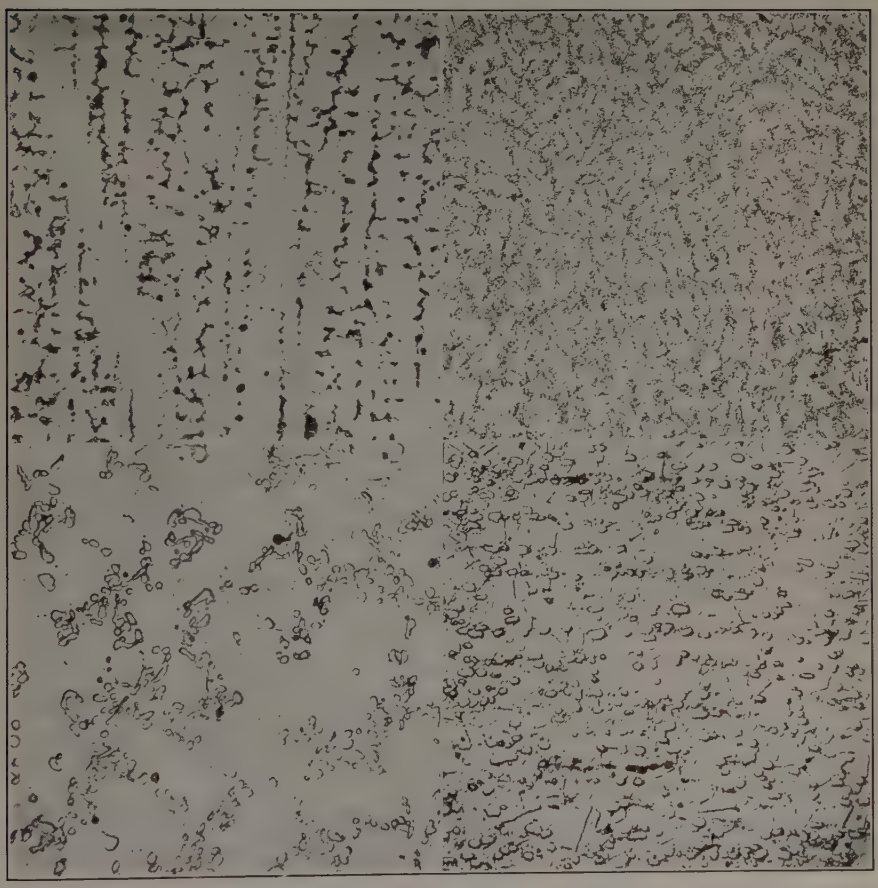

FIG. 5.—CAST NICKEL-MOLYBDENUM-IRON ALLOY. × 100.
FIG. 6.—FORGED NICKEL-MOLYBDENUM-IRON ALLOY. × 100.
FIG. 7.—FORGED NICKEL-MOLYBDENUM-IRON ALLOY. × 500.
FIG. 8.—NICKEL-MOLYBDENUM-IRON SHEET HOT-ROLLED TO 0.040 IN. THICK AND REHEATED TO 1050° C. × 500.

Studying the effect of adding copper to this nickel-silicon-aluminum alloy, it was found that from 2.5 to 3 per cent. copper gave a finer grained and considerably stronger alloy. Metallographic examination led to the idea that the sum of the silicon and aluminum should not exceed 12 per cent. if the formation of certain intermetallic compounds was to be

avoided. The aluminum was diminished but the copper was retained, and favorable results followed at once. A nickel alloy containing approximately 10 per cent. silicon, 1.5 to 2 per cent. aluminum, and 3 per cent. copper makes strong, tough castings which are quite acid resistant. The alloy is not workable but is machinable with difficulty. Its Brinell hardness is about 364 and while this can be reduced to somewhat under 300 by heating for several hours at 1050° C. and quenching in water, it has not been found feasible to machine the alloy with anything but tungsten carbide tools. These tools offer a means of performing simple machining operations, such as facing off a flange, when grinding is not convenient. Table 2 gives some of the physical properties of this alloy. The transverse tests were made on standard arbitration bar castings and loaded midway between supports 12 in. apart. A breaking load of 5000 lb. with a deflection of 0.070 to 0.080 in. is considerably above the usual values for cast iron and is about five times that of the commercial iron-silicon alloys now in use for acid-resisting purposes.

While the resistance of this alloy to hydrochloric acid is not quite so high as that of nickel-molybdenum-iron, it is still considerably above that of most commercial alloys. In 10 per cent. HCl at 70° it loses 0.00018 g. per sq. cm. per hr., corresponding to a penetration of 0.0066 in. per month; but, unlike the nickel-molybdenum-iron alloy, it is somewhat less resistant to stronger acid. Towards sulfuric acid at 70°, it shows practically the same resistance as nickel-molybdenum-iron, but at the boiling points it has better resistance throughout the range of acid concentrations investigated than nickel-molybdenum-iron at the same concentrations. In acetic and phosphoric acids, the alloy also compares favorably with nickel-molybdenum-iron.

TABLE 2.—*Physical Properties of Nickel-silicon-copper-aluminum Alloy*

Specific gravity	7.8
Weight per cu. in., lb	0.280
Weight per cu. ft., lb	484
Melting point	1160° C.
Coefficient of expansion, in. per ° C	11.6×10^{-6}
Thermal conductivity per ° C., cal. per sq. cm. per cm. per sec	0.005
Electrical resistivity, microhms per cm. cube at 24° C	113.0
Temperature-resistance coefficient per ° C	0.0013
Electrical conductivity, per cent. that of copper at 24° C	1.6
Shrinkage, sand casting, in. per ft	¼
Transverse breaking load, 12 in. span, lb	5000
Deflection, in	0.070–0.080
Modulus of rupture	78,200
Brinell hardness	364

Photomicrographs of the nickel-silicon-copper-aluminum alloy are shown in Figs. 9 and 10. This is rather a complex structure in the cast

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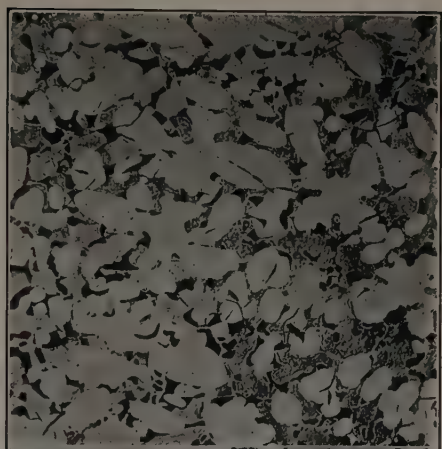

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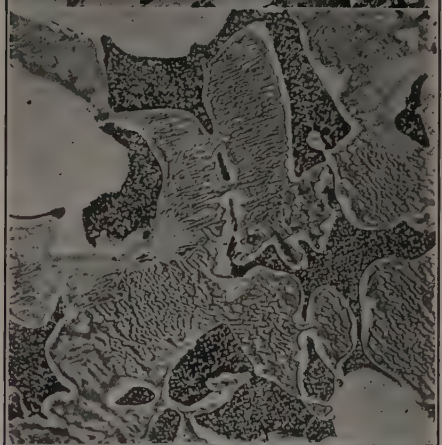

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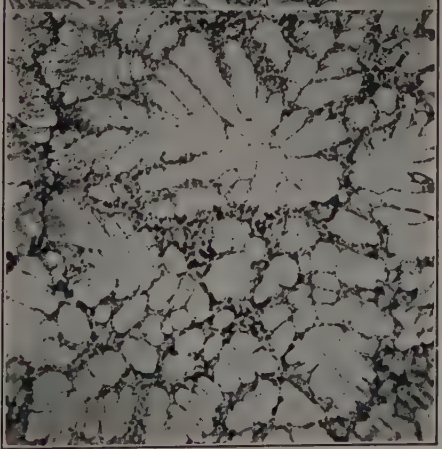

FIG. 9.—CAST NICKEL-SILICON-COPPER-ALUMINUM ALLOY. × 100.
FIG. 10.—CAST NICKEL-SILICON-COPPER-ALUMINUM ALLOY. × 500.
FIG. 11.—OXYACETYLENE WELD IN CAST NICKEL-SILICON-COPPER-ALUMINUM ALLOY. × 100.

state, consisting of three components, a solid solution and two eutectics. Figs. 9 and 10 show the structure at different magnifications and Fig. 11 shows the structure of an oxyacetylene weld made in this alloy. The same three constituents appear in Fig. 11 as in Fig. 9, but the change in the rate of cooling has caused a change in the appearance. Because of the silicon and aluminum present, this alloy is a little more difficult to weld with the oxyacetylene torch than the nickel-molybdenum-iron alloys, but it can be done satisfactorily with the aid of a special flux.

The laboratory stage in the development of these alloys is largely complete but laboratory corrosion tests cannot be considered as more than an indication of the value of an acid-resisting alloy. The ultimate criterion must be the test under plant conditions and such tests are now being made by various chemical companies. It is not expected that these alloys will displace other corrosion-resisting alloys, for the requirements of the chemical industry vary widely both as to properties and permissible cost, but it is hoped that they will meet certain needs, particularly in connection with hydrochloric acid, which have not hitherto been met satisfactorily by other materials.

Acknowledgment

The writer wishes to express his appreciation to F. M. Becket, president of the Union Carbide and Carbon Research Laboratories, Inc., for his stimulating interest in this research. He also wishes to thank his associates, W. B. Miller, C. R. Bishop, Russell Franks, and C. E. Plummer, for their assistance in carrying out the work.

DISCUSSION

N. B. Pilling, Bayonne, N. J. (written discussion).—Perhaps one of the things which most impress the casual reader of the literature of corrosion-resistant alloys is the contrast between the great quantity of detailed and specific information available and the great lack of generalizations which codify even a portion of this information in suggestive form. Attempts to formulate such generalizations have not been lacking but few of these rules have proved durable. Concealed among other useful information in this paper by Mr. Field is evidence that another hoary rule must go by the board; namely, that which states that high resistance to corrosion is an attribute only of the simple metals or of homogeneous solid-solution alloys. While it is true that the most familiar corrosion-resistant alloys are of this type, it requires only a glance at Mr. Field's photomicrographs (Figs. 8 and 10, for example) to realize that under some conditions a highly heterogeneous alloy may display a great resistance to attack. The value of generalized deductions lies in their power to guide with confidence in new fields and to avoid, with equal confidence, nonpertinent effort. It would seem that the future investigator could not safely consider, *a priori*, structural complexity as being incompatible with resistance to corrosion.

Would Mr. Field agree that the particular excellence of these high-molybdenum content alloys in hydrochloric acid solutions is closely related to the fact that molybdenum is one of the very few metals forming water-insoluble chlorides, and that the

absence of destructive galvanic action between phases is due to a highly effective film formation?

B. E. Field.—I agree with Mr. Pilling that the insolubility of molybdenum chloride in water has much to do with the excellent resistance to hydrochloric acid shown by these high-molybdenum alloys. His suggestion that film formation accounts for the absence of destructive galvanic action between the phases also seems to be a plausible explanation.

Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids

By H. A. Bedworth,* Waterbury, Conn.

(New York Meeting, February, 1929)

Alloys of copper and silicon have been known for one hundred years or more but the commercial development of this type of alloy has taken place during the past few years. In 1905, Sperry[1] proposed the use of copper-silicon alloys for springs and other purposes for which copper-tin bronzes were used. Some attention was given to this proposal at the time but no one succeeded in producing a practical alloy containing more than a fraction of a per cent. of silicon.

The equilibrium relations of the copper-silicon system were studied first by Rudolfi[2] and later by Sanfourche[3] and Corson.[4] The constitution of the system has also been recently investigated by Matuyama,[5] and in the laboratories of the American Brass Co. by Smith.[6] Some of the physical properties of the copper-silicon alloys have been investigated by Norbury[7] and by Geiss and Van Liempt.[8]

Summarizing the results of various investigators of the constitution of copper-silicon alloys, the solubility reaches its maximum value, 6.7 per cent. silicon, between 721° and 782° C. At 852° C. the solubility is 5.25 per cent., while at 400° C. it is only 4.1 per cent. silicon.

The copper-silicon alloy begins to get so hard at about 3 per cent. silicon that it is difficult to manage. It was found by Jacobs that the addition of manganese to this alloy considerably improved the working

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* Research Laboratory, The American Brass Co.

[1] E. S. Sperry: Silicon-copper for Spring Wire. *Brass World* (1905) **1,** 413.

[2] E. Rudolfi: Die Silicide des Kupfers. *Ztsch. anorg. Chem.* (1907) **53,** 216.

[3] M. A. Sanfourche: Sur les Alliages Cuivre-silicium. *Rev. Mét.* (1919) **16,** 246.

[4] M. G. Corson: Copper Alloy Systems with Variable Alpha Range. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 435.

Merit in Copper-silicon Alloys. *Iron Age* (1927) **119,** 353.

[5] K. Matuyama: On the Equilibrium Diagram of the Copper-silicon System. *Sci. Repts.* Tohoku Imp. Univ. [1] (1928) **17,** 665.

[6] C. S. Smith: The Alpha Phase Boundary of the Copper-silicon System. *Jnl.* Inst. Met. (1928) Advance Copy No. 476.

The Constitution of the Copper-silicon System. See p. 414.

[7] A. L. Norbury: The Hardness of Certain Copper Alpha-solid Solutions. *Jnl.* Inst. Metals (1923) **29,** 423.

[8] W. Geiss and J. A. M. Van Liempt: Copper-silicon Alloys of High Copper Content. *Ztsch. anorg. Chem.* (1927) **168,** 31.

qualities and a patent covering alloys with copper, silicon, and manganese was issued to him.[9]

The addition of silicon and manganese is one of the most effective means of hardening and strengthening copper. At the same time these additions increase its general resistance to corrosion.

It was in connection with the further commercial development of this alloy that the investigation described in this paper was carried out. The alloys considered were within the range of practical limits; that is, silicon varied from 0.5 to 4.0 per cent., the silicon-manganese ratio being held constant at approximately 3:1.

Material Investigated

The material used for this investigation was in the form of both hard-drawn and annealed wires, 0.183 in. dia. The hard wires were cold-drawn to size from wire annealed at 0.365 in. dia., a reduction of 6 B. & S. numbers. The annealed wires were annealed at 750° C. for ½ hr., followed by air-cooling at room temperature. The composition of the alloys is shown by Table 1.

Table 1.—*Composition of Alloys*

Sample Number	Copper, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.	Iron, Per Cent.
99979–7	99.31	0.57	0.22	0.07
182–7	99.10	0.78	0.27	0.05
182–6	98.42	1.14	0.40	0.07
99975–5	97.96	1.61	0.51	0.08
182–4	97.27	2.12	0.68	0.11
182–3	96.45	2.56	0.87	0.15
99971–2	95.83	3.04	1.07	0.16
182–2	96.03	3.17	0.89	0.10
182–1	94.60	4.01	1.21	0.20

Table 2.—*Rockwell Hardness Tests*

Sample Number	Silicon, Per Cent.	Annealed	Hard
99979–7	0.57	−17	72
182–7	0.78	−14	76
182–6	1.14	− 9	82
99975–5	1.61	−13	102
182–4	2.12	3	98
182–3	2.56	12	101
99971–2	3.04	35	89
182–2	3.17	25	102
182–1	4.01	68	105

[9] C. B. Jacobs: U. S. Patent No. 1539260, May 26, 1925.

FIG. 1.—Si 0.57, Mn 0.22 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.
FIG. 2.—Si 0.78, Mn 0.27 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.
FIG. 3.—Si 1.14, Mn 0.40 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.
FIG. 4.—Si 1.61, Mn 0.51 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.
FIG. 5.—Si 2.12, Mn 0.68 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.
FIG. 6.—Si 2.56, Mn 0.87 PER CENT. ANNEALED AT 750° C. FOR ½ HR. × 75.

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Fig. 7.—Si 3.04, Mn 1.07 per cent. Annealed at 750° C. for ½ hr. × 75.
Fig. 8.—Si 3.17, Mn 0.89 per cent. Annealed at 750° C. for ½ hr. × 75.
Fig. 9.—Si 4.01, Mn 1.21 per cent. Annealed at 750° C. for ½ hr. × 75.

Rockwell hardness tests of the specimens are shown in Table 2. Tests were made with 1/16-in. dia. ball, 100-kg. load, "B" scale.

The structures of annealed specimens are shown by Figs. 1 to 9. The grain size of the annealed specimens increases with decreasing silicon and manganese content.

Testing Procedure

Corrosion tests were made by alternate immersion in dilute hydrochloric acid at room temperature and dilute sulfuric acid at 60° C. The acid concentration in each case was 10 per cent. by weight. Specimens were raised and lowered by mechanical means, the immersion cycle being 1½ minutes in the solution followed by 1½ minutes in the air. The total time of test was 216 hr. The specimens were immersed in a horizontal position to a depth of about 2 in. below the top of the solution. Glass battery jars, 6 by 9 by 12 in., holding 8 liters of solution, were used as containers and 12 specimens were tested in each jar. The hot solution was maintained at 60° C., ± 1° C., by means of a circulating water bath, the temperature of which was controlled by an electric thermostat. Tests were made in triplicate, using specimens 8 in. long.

Relative corrosion was determined by measuring loss in weight, tensile strength, and elongation. The corrosion of all alloys was fairly uniform and pitting was too slight to warrant measurement.

The test described is of the accelerated type, acceleration being effected by complete aeration of the film of corroding liquid adhering to the test pieces, as well as by alternate wetting and drving.

Results of Tests

Loss in weight is shown by Table 3 and Fig. 10.

Table 3.—*Loss in Weight*

Grams per Sq. In. at End of 216 Hr.

Silicon, Per Cent.	10 Per Cent. HCl Room Temperature		10 Per Cent. H_2SO_4 60° C.	
	Hard	Annealed	Hard	Annealed
0.57	0.99	0.89	1.76	1.60
0.78	0.84	0.75	1.75	1.68
1.14	0.76	0.63	1.78	1.45
1.61	0.70	0.49	1.58	1.15
2.12	0.73	0.42	1.39	0.78
2.56	0.67	0.38	1.58	0.85
3.04	0.72	0.41	1.37	0.64
3.17	0.69	0.42	1.37	0.72
4.01	0.69	0.45	1.30	0.52

Tensile strength and elongation before and after corrosion are shown by Table 4 and Figs. 11 and 12. Loss in tensile strength and elongation expressed in per cent. of original properties are shown by Table 4 and Figs. 13 and 14.

TABLE 4.—*Loss in Tensile Strength and Elongation*

Silicon, Per Cent.	Tensile Strength, Lb. Per Sq. In.			Elongation in 2 In.		
	Original	Corroded	Loss, Per Cent.	Original	Corroded	Loss, Per Cent.
10 Per Cent. HCL—Room Temperature						
Hard Wires						
0.57	66,200	55,600	16.0	7.0	7.0	0
0.78	65,430	59,000	9.8	7.7	7.5	3
1.14	78,330	68,400	12.7	7.5	7.2	4
1.61	92,870	82,600	11.1	6.8	6.5	4
2.12	118,900	106,200	10.7	7.0	6.3	10
2.56	129,830	116,000	10.6	5.3	5.5	0
3.04	139,300	124,000	11.0	4.3	4.7	0
3.17	141,900	124,500	12.3	6.0	5.7	5
4.01	155,500	126,600	18.6	0.8	1.3	0
Annealed Wires						
0.57	36,000	32,800	8.9	46.8	44.2	6
0.78	38,300	32,100	16.2	44.7	46.7	0
1.14	39,630	35,400	10.7	48.5	47.2	3
1.61	42,470	40,600	4.4	44.5	42.2	5
2.12	48,500	45,700	5.8	55.8	54.2	3
2.56	57,530	51,700	10.1	55.5	58.5	0
3.04	64,700	60,900	5.9	56.0	54.2	3
3.17	63,230	59,000	6.7	58.2	57.2	2
4.01	78,470	72,800	7.2	46.2	44.2	9
10 Per Cent. H_2SO_4—60° C.						
Hard Wires						
0.57	66,200	51,000	23.0	7.0	5.8	17
0.78	65,430	50,300	23.2	7.7	6.3	18
1.14	78,330	58,400	25.5	7.5	5.7	24
1.61	92,870	72,000	22.5	6.8	5.5	19
2.12	118,900	98,000	17.6	7.0	5.3	24
2.56	129,830	103,300	20.4	5.3	4.5	15
3.04	139,300	113,000	18.9	4.3	4.3	0
3.17	141,900	113,000	20.4	6.0	4.2	30
4.01	155,500	110,000	29.2	0.8	0.8	0
Annealed Wires						
0.57	36,000	29,900	17.0	46.8	40.3	14
0.78	38,300	28,000	26.9	44.7	41.0	8
1.14	39,630	31,000	21.8	48.5	39.3	19
1.61	42,470	35,900	15.5	44.5	36.7	18
2.12	48,500	43,300	10.7	55.8	45.7	18
2.56	57,530	48,700	15.4	55.5	55.2	0.5
3.04	64,700	59,300	8.4	56.0	49.8	11
3.17	63,230	58,000	8.3	58.2	51.3	12
4.01	78,470	73,300	6.6	46.2	37.0	20

Discussion of Results

In presenting and discussing results, the alloys are referred to according to silicon content, as this is the most important factor under consideration, with regard to the composition of the alloy. It should be borne in mind that these alloys contained also manganese in the ratio 3 silicon:1 manganese.

The loss in weight in both hydrochloric and sulfuric acids (Fig. 10) decreases rapidly from 0.5 to 2 per cent. silicon. In hydrochloric acid the loss in weight is practically constant with alloys containing from 2 to 4 per cent. silicon, while in sulfuric acid it decreases slightly as the silicon

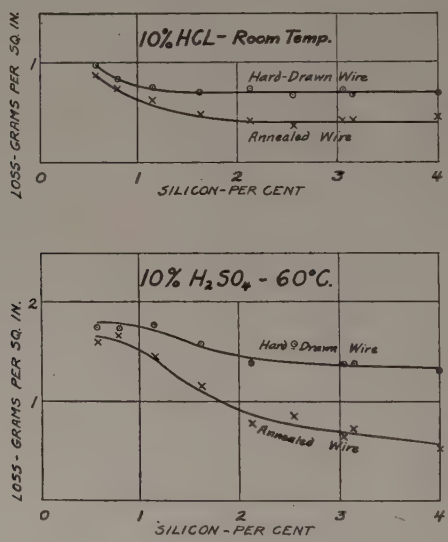

Fig. 10.—Loss in weight after corrosion.

content increases from 2 to 4 per cent. The annealed specimens of higher silicon content (2 to 4 per cent.) show much less loss in weight than the hard specimens, while with decreasing silicon content (2 to 0.5 per cent.) the loss of the annealed specimens approaches that of the hard-drawn specimens.

The tensile strength of hard-drawn specimens before corrosion (Fig. 11) increases from 66,000 to 155,000 lb. per sq. in. The curves representing tensile strength of corroded hard specimens parallel roughly those of original strength from 0.5 per cent. to approximately 2 per cent. silicon, and show divergence above 2 per cent. silicon, the rate of divergence increasing above 3 per cent. The curves representing tensile strength of annealed wires after corrosion are practically parallel to those representing original strength.

The elongation of corroded specimens (Fig. 12) parallels roughly the original elongation.

The relative effects of corrosion as measured by loss of strength and elongation are presented in a more direct manner by Figs. 13 and 14, which show graphically the percentage loss based on original tensile strength and elongation. The percentage loss of strength of hard specimens decreases as the silicon content increases from 0.5 to 2 per cent.;

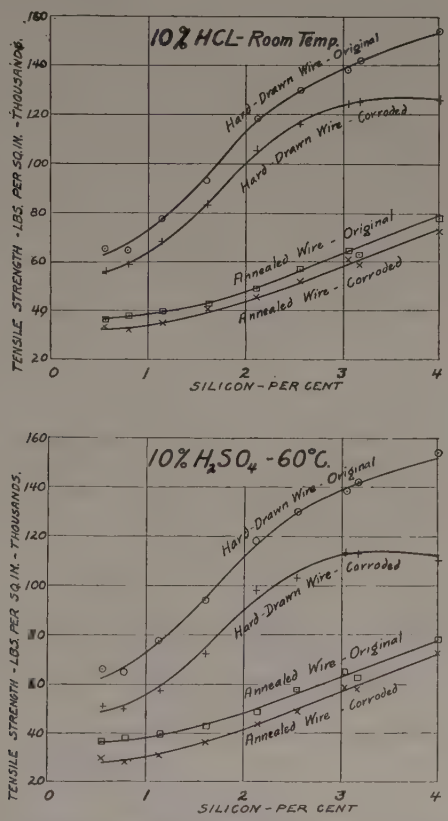

FIG. 11.—TENSILE STRENGTH BEFORE AND AFTER CORROSION.

is practically constant from 2 to 3 per cent., reaching a minimum at approximately 2.5 per cent. silicon; and increases rapidly from 3 to 4 per cent. silicon. The loss of strength of annealed specimens in hydrochloric acid decreases from 0.5 to 2 per cent. silicon and becomes constant as the silicon content increases from 2 to 4 per cent. In sulfuric acid the loss in strength decreases regularly as the silicon content increases from 0.5 to 4 per cent.

Curves showing percentage loss in elongation (Fig. 14) indicate that the composition of these alloys, within the limits of these tests, was

without influence on the loss in elongation due to corrosion. It is appreciated that the curves representing elongation are more or less approximations, as the experimental error in individual determinations was unfortunately large, due to the necessity of using relatively short specimens.

The sharp rise in the curves representing percentage loss in strength of hard-drawn wires containing more than 3 per cent. silicon (Fig. 13) is

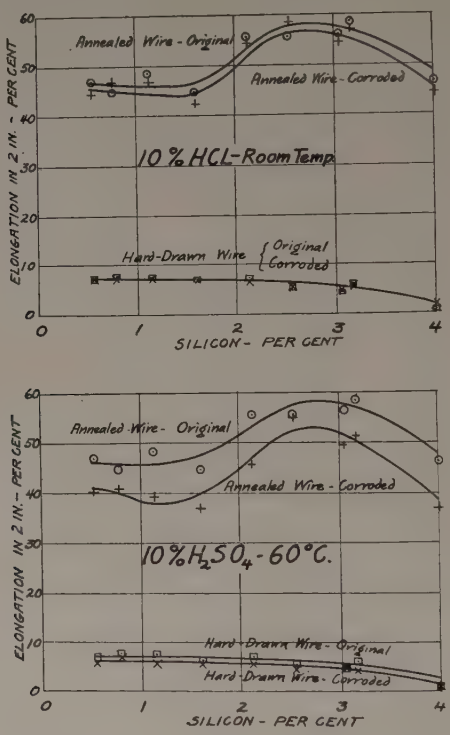

FIG. 12.—ELONGATION BEFORE AND AFTER CORROSION.

extremely interesting, and suggests the possibility of difference in constitution of the alloy containing 4 per cent. silicon. Examination under the microscope at high powers revealed small undissolved particles of grayish blue Mn_2Si in both hard and annealed specimens containing 4.01 per cent. silicon and 1.21 per cent. manganese. Figs. 15 and 16, magnification 500, illustrate the structures of specimens with Mn_2Si inclusions. No inclusions of Mn_2Si were visible in specimens containing 3.17 per cent. silicon and 0.89 per cent. manganese. Galvanic action, due to the presence of Mn_2Si inclusions in the hard-drawn specimens containing 4 per cent. silicon, may possibly explain the relatively greater loss of strength after corrosion of this alloy. Annealing apparently

counteracts the harmful effect of these inclusions. It should be noted particularly that the determination of tensile strength shows a definite

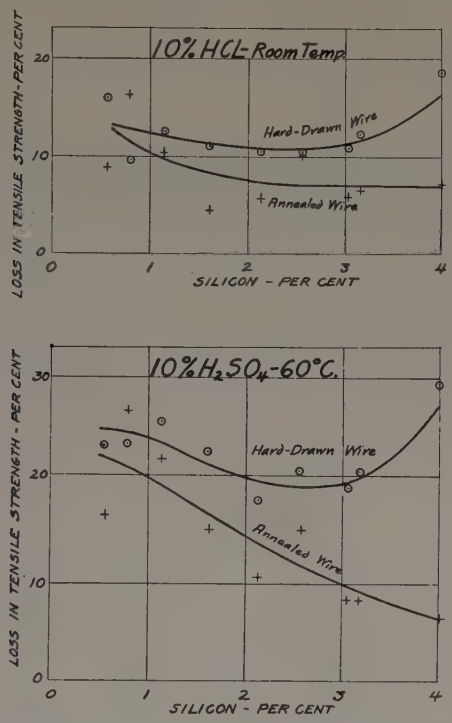

FIG. 13.—LOSS IN TENSILE STRENGTH AS PERCENTAGE OF ORIGINAL STRENGTH.

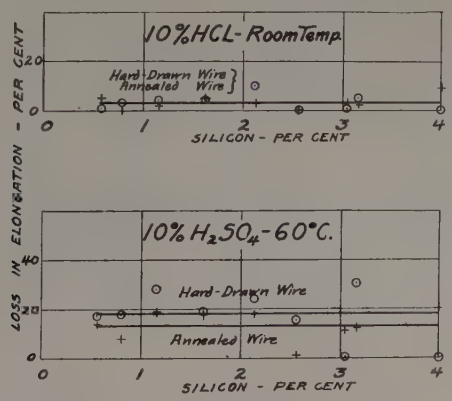

FIG. 14.—LOSS IN ELONGATION AS PERCENTAGE OF ORIGINAL ELONGATION.

difference in the relative corrosion of alloys containing 3 and 4 per cent. silicon, respectively, which would be lost sight of entirely if only determination of loss in weight were relied on as a criterion.

The marked difference in relative corrosion of hard and annealed specimens of higher silicon content is of particular interest, as this difference has not been observed to occur generally in tests of other commercial copper alloys. Our present knowledge does not afford a satisfactory explanation of this phenomenon and it is hoped that further work will shed light on this point.

15

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FIG. 15.—Si 4.01, Mn 1.21 PER CENT. HARD-DRAWN 6 B. & S. NUMBERS. LIGHTLY ETCHED. × 500.

FIG. 16.—Si 4.01, Mn 1.21 PER CENT. ANNEALED AT 750° C. FOR ½ HR. LIGHTLY ETCHED. × 500.

SUMMARY

1. Corrosion tests of copper-silicon-manganese alloys, varying in composition from 0.5 per cent. silicon, 0.2 per cent. manganese to 4.0 per cent. silicon, 1.2 per cent. manganese (silicon-manganese ratio 1:3) in

hydrochloric and sulfuric acids have shown that additions of silicon and manganese up to 3 and 1 per cent., respectively, materially increase the corrosion resistance of the alloy to these acids. Little further benefit is realized by additions beyond this amount.

2. Hard-drawn wires containing more than 2 per cent. silicon showed decidedly greater loss by corrosion than annealed wires of the same composition. The loss of annealed wire approached that of hard wire as the silicon content decreased from 2.5 to 0.5 per cent.

3. Hard-drawn wires containing 4 per cent. silicon and 1.2 per cent. manganese showed much greater loss in tensile strength after corrosion than did hard-drawn wires containing 3.2 per cent. silicon and 0.9 per cent. manganese. It was found by examination under the microscope that the 4 per cent. alloy contained small undissolved particles of Mn_2Si whereas the 3 per cent. alloy did not, which may explain this effect. Annealed wires of the 4 per cent. alloy also showed Mn_2Si inclusions, but showed practically the same corrosion rate as the 3 per cent. alloy. Annealing apparently counteracts the harmful effect of Mn_2Si inclusions.

4. Corrosion testing procedure is described in which not only loss in weight but also loss in tensile strength and elongation has been determined. This method of procedure has been found satisfactory for testing various nonferrous alloys and series of alloys. In the study of alloys which are heterogeneous, loss in weight alone has been found to be an unreliable criterion, and in such cases the determination of effect of corrosion on physical properties is most essential in the estimation of relative corrosion resistance.

DISCUSSION

D. E. Ackerman, Bayonne, N. J. (written discussion).—It is not the purpose of the paper just read to discuss the technique of corrosion testing; at the same time the conclusions are based upon the results of corrosion tests and are valid only in so far as the variables affecting corrosion processes are properly controlled. In the present case several elements of control in testing seem to be lacking.

Dissolved oxygen in the corroding solution is now recognized as one of the most important variables in corrosion testing. The author has used the alternate immersion test, in which the specimen is periodically withdrawn from the body of corroding solution and exposed to the air while wet, the assumption being that the film of solution on the specimen will absorb air. The writer has found that if, as in the author's experiments, a copper wire is dipped horizontally into a 10 per cent. hydrochloric acid solution at room temperature (18° C.) and is then held in the air the solution is by no means distributed as an approximately even film, and after 1.5 mm. the wire will be almost if not quite dry. During this time the outer layers of the solution film have evaporated, and the concentration of compounds in the film has proportionately increased. This produces at least two results: (1) the concentration and nature of the solution film next to the specimen may change considerably and over an unknown range from the concentration and nature of the original test solution, so that the conditions responsible for the corrosion are no longer clearly defined; (2) the increase in concentration of the solutes in the film generally lowers the amount of

oxygen which is soluble in the film of solution. To be conservative, we may assume that only one-half of the solution film evaporates during the exposure of the specimen to air; a 10 per cent. solution of sulfuric acid would then become concentrated to 20 per cent., provided none of the solute volatilizes, and at 25° C. this change in acid concentration would reduce the maximum oxygen solubility in the film from about 0.039 to 0.031 g. per liter,[10] a reduction of about 20 per cent., and the data available indicate that the corresponding change in oxygen solubility in hydrochloric acid is of the same order of magnitude. This suggests that the oxygen content of the solution film on the alternate immersion specimen at the time of reimmersion may easily be appreciably lower than that of the solution in contact with a specimen constantly totally immersed in a moving air-saturated solution.

The amount of oxygen that will dissolve in the film of solution on the specimen exposed to the air thus depends, among other things, upon the concentration and rate of evaporation of the film itself. Some other factors influencing the oxygen content of the solution film are the presence of air currents and the atmospheric temperature and humidity, variables which the author apparently did not control. That this lack of control constitutes a practical objection to the technique employed is evidenced by the report of Committee B-3 of the American Society for Testing Materials for 1927. The report, discussing the causes for the wide variation in results obtained by different laboratories, says,[11] ". . . the temperature and humidity of the air over the apparatus gave rise to great variations. . . . It was apparent that the samples should either be positively dry in as short a time as possible or else kept positively moist for the entire part of the cycle in which they were suspended in the air. . . . It was decided to adopt, for the present, the policy of using a higher temperature of solution, thereby resulting in the almost immediate and complete drying of the samples." The temperature adopted was 60° C., the same as that used by Mr. Bedworth in the sulfuric acid tests. This procedure largely eliminates variations due to the affect of atmospheric temperature and humidity but, by subjecting the specimen to the action of a corrodant whose nature and concentration changes over an even wider range than at low testing temperature, aggravates the two objectionable features of the test which were mentioned in the second paragraph of this discussion. Another objection to the practice of maintaining the solution at a high temperature without also controlling air currents and atmospheric temperature is that the temperature of the specimen at the time of reimmersion will not be constant but will fluctuate with the atmospheric temperature, and this leads to still further difficulty in closely defining the test conditions, since both the specimen temperature and the nature and concentration of the solution film next to the specimen are varying simultaneously, the latter over a range whose limits can be only approximately defined.

Another variable which the author seems to have neglected is the composition of the atmosphere into which the specimens are raised. Gases other than nitrogen and oxygen will also be absorbed in proportion to their respective partial pressures. Gases such as hydrogen sulfide, sulfur dioxide, ammonia, etc., are usually present in laboratory atmospheres and it has been my experience that small quantities of such compounds may radically change the nature of the attack. On this point the report of Committee B-3 says: "Control of laboratory atmosphere is essential."

While the writer has not made a critical study of the alternate immersion test, it appears to him that in order to use this test to obtain data under accurately defined conditions all of the variables encountered in total immersion testing must be con-

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[10] O. B. J. Fraser, D. E. Ackerman and J. W. Sands: Controllable Variables in the Quantitative Study of the Submerged Corrosion of Metals. *Ind. & Eng. Chem.* (1927) **19**, 332.

[11] *Trans.* A. S. T. M. (1927 **27**, I, 283–284.

trolled and, in addition, such other variables (atmospheric temperature, humidity and air currents) as tend to alter the characteristics of the film of solution on the specimen must also be controlled. The necessity for the control of this latter class of variables, which seems inherent in the method of test, gives rise to serious experimental difficulties which are not encountered in the total immersion test as described by Fraser, Ackerman and Sands,[12] and by Pilling and Ackerman,[13] and the writer would like to ask the author to express his opinion of the importance of the variables discussed above as they affect the results obtained in alternate immersion testing. In any event, the work of Thompson and McKay[14] and others makes it seem desirable to control the oxygen content of the bath of solution and to provide for movement of the solution relative to the specimen. Motion is especially important in the study of high-copper alloys, as they are unusually susceptible to ionic polarization.

Tests run at an uncontrolled "room temperature" are difficult to interpret, especially when, as in the paper under discussion, no record of the temperature is available. Experience indicates that what is called "room temperature" is actually an ill-defined range of temperature. In controlled total immersion tests we have found that certain types of alloys are so sensitive to testing temperature in the "room temperature" range that a small drop in the controlled temperature within this range, such as may take place during the night, suffices to change the alloys from a freely corroding to an almost or completely resistant condition. In making corrosion tests on alloys intended for service over a range of temperature it is usually better to run tests at a series of temperatures over the range to be encountered, for to show that the effect of temperature is negligible, than to attempt to duplicate poorly defined service fluctuations.

No mention is made of precautions taken to assure a constant concentration of testing solution over the long test period.

The writer assumes that the weight losses and tensile data are average figures from the triplicate tests mentioned by the author and would like to ask what variation from this average was shown by the individual members of each trio of specimens.

On page 161 it is stated, "At the same time these additions (silicon and manganese) increase its general resistance to corrosion." Evidently both silicon and manganese contribute to the increased corrosion resistance of these alloys, and data on the effect of each of the elements in question in the absence of the other would be of interest.

It is unfortunate that the author did not include copper in his tests, as this metal would have served as a reference point which could be easily obtained and accurately reproduced.

C. G. Fink, New York, N. Y.—These intermittent corrosion tests are of much more value than our standard salt-spray test, and it is true that one must take care of the change in concentration of the solution. Parallel tests should be made to get a direct check.

Some years ago we had occasion to investigate the copper-silicon-manganese alloys. We carried the silicon even further than shown in Fig. 10. We found a minimum loss around 18 or 20 per cent. silicon. The alloy developed[15] into a commercial anode and has been in operation for 10 years. The solution contains sulfuric, nitric and hydrochloric acids. The alloy is much less soluble than lead.

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[12] O. B. J. Fraser, D. E. Ackerman and J. W. Sands: *Op. cit.*

[13] N. B. Pilling and D. E. Ackerman: Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids. See page 248.

[14] J. F. Thompson and R. J. McKay: Control of Motion and Aeration in Corrosion Tests. *Ind. & Eng. Chem.* (1923) **15**, 114.

[15] C. G. Fink: U. S. Patents 1441567, 1441568. Jan. 9, 1923.

C. S. Smith, Waterbury, Conn.—I would like to inquire of Dr. Fink if the 20 per cent. copper-silicon alloys he mentioned contain an appreciable amount of iron or other elements likely to affect the corrosion. I have found that practically pure copper-silicon alloys containing more silicon than the eutectic (16 per cent. silicon), disintegrate on exposure to the atmosphere for a period of about one year.

C. G. Fink.—I hope they are stable. They have been in a solution 24 hr. a day for 10 years. Originally we started with pure silicon in making the alloy; now we use ferrosilicon because that is cheaper than silicon; accordingly, the anode contains iron.

H. A. Bedworth.—The effects of the factors mentioned by Mr. Ackerman have been definitely appreciated, and it has been realized that the control of these factors may play an important part in the reproducibility of results by corrosion tests. However, the tests described in this paper were carried out with the object of determining the relative corrosion resistance of members of a series of alloys, subjecting them all to practically identical conditions. The type of test was chosen in the beginning as being as nearly as possible a duplication in the laboratory of what actually takes place in an important type of service; that is, alternate wetting and drying by acid solutions. In a test of comparative nature, such as the one described, the control of certain factors common to all specimens may be omitted without in any way impairing conclusions as to relative corrosion resistance.

The comparison of these tests with those of the American Society for Testing Materials is entirely beside the point, as the implied analogy does not exist. The A. S. T. M. tests were cooperative in nature and were carried out with the object of duplicating results in various laboratories and also of standardizing corrosion testing procedure. With respect to duplication of results by this type of test in various laboratories, where climatic conditions might differ considerably, I quite agree that the control of certain factors such as temperature and humidity of the atmosphere surrounding the testing apparatus would be important.

The method of maintaining concentration of solutions was not mentioned in the paper. The concentration of sulfuric acid was maintained by the addition of distilled water by means of an automatic syphon to replace water lost by evaporation. No additions were made to hydrochloric acid as tests in this acid were at room temperature and loss by evaporation was not significant. Referring to the text, the volume of 8 liters of solution to each 12 specimens was more than ample to avoid appreciable depletion of the solution by chemical reaction with metals.

With regard to the variation among individual results from each trio of specimens, the loss in weight of any individual specimen was within 10 per cent. of the average of the three results, the variation in the great majority of cases being less than 5 per cent. The individual loss in tensile strength showed variation of less than 5 per cent. from the average of the trio, in the majority of cases being 1 or 2 per cent.

It would be interesting, as Mr. Ackerman has said, to know the effects of silicon and manganese separately. That is still another problem and more than was attempted in this particular investigation. Copper was omitted, not intentionally, but because interest was centered particularly in the alloys of higher silicon content, those above 2 per cent. silicon, on account of their improved physical properties. From a standpoint of completing the data, however, we regret that copper was not also included.

Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk

By Robert J. McKay,* O. B. J. Fraser,* and H. E. Searle,* New York, N. Y.

(New York Meeting, February, 1929)

The practical study of corrosion requires consideration of its economic aspects. It must be based on sound scientific principles, but it should be borne in mind that probably the most important object of a corrosion test is to determine what metal in corrosion-resisting construction will produce the greatest operating profit. Thus the corrosion test must be directly connected with money values or it is not a practical corrosion test. This, perhaps unusual, connection between corrosion and economics is partially due to the fact that corrosion deals only with the time factor or duration of equipment, and it is almost the only test which deals with this feature.

In these statements a departure is made from the academic definition of the word corrosion and it is done deliberately. The use of the term corrosion is unusual. It is as though we spoke of a tensile test as a "breaking" test. We are not interested primarily in the break but in the strength of the metal. There is no English word which expresses our main interest in corrosion-testing, but let us have clearly in mind that we make *corrosion tests* to *prevent corrosion.* Our real interest is in this corrosion-prevention, not in the corrosion.

Previous to 1922, it was common comment that "it is impossible to determine the course of corrosion by laboratory testing." This statement was true at that time in that the technique of laboratory testing for corrosion resistance was so vague that tests in the laboratory gave untrue results almost as often as true ones. This was so, even in the simple case of determining which one of two metals better resists a given solution. While this is no longer true the number of misleading "corrosion tests" still being ground out by laboratories is too large in the light of our present knowledge. There are two important features of corrosion testing whose neglect is a large contributing factor to misleading results: (1) The economic relations of the corrosion tests to other tests; (2) testing technique.

Regarding economic relations J. F. Thompson[1] has said: "The use of any particular metal is rarely based upon the sole property of resistance to corrosion. In fact, I should like to venture the assertion

* Development and Research Department, International Nickel Co.

[1] J. F. Thompson: A Practical Aspect of the Corrosion Problem. *Trans.* Am. Electrochem. Soc. (1921) **39**, 213.

that resistance to corrosion alone, although always a necessary factor, is quite frequently not the determining one of practical serviceability in any particular anticorrosion piece of construction, but some other property often entirely unrelated." Dr. Thompson outlined some of the usual determining factors, other than corrosion. This paper illustrates these factors for milk on nickel and monel metal and they are summarized in Part III.

Quoting again,[2] "Corrodibility is not a specific property, capable of exact definition, but may depend upon the greatest variety of incidental conditions." That is, corrosion or "corrosion resistance" is not a property of a metal as is strength or melting point. Such properties are determinable by properly designed tests which are subject to standardization. Corrosion experiments from their very nature are more complicated and will never be standardized in the sense of adapting one test to all types of corrosion.

This brings us to the other main feature, testing technique.

In 1922 and the following years papers have been published which so clarify the "incidental conditions" on which corrosion depends that these conditions are no longer impossible to control in good corrosion-testing practice. This does not mean that we are at or near the ultimate in the knowledge of the scientific facts which underly corrosion testing, or that there are no types of corrosion whose course cannot be predicted in the laboratory. This is far from true. But it is true now that the greater number of types of corrosion are susceptible of accurate reproduction in the laboratory and the principal scientific facts whose vagueness made the phenomena of corrosion enigmatical up to 1922 are so well understood at present that a relatively large proportion of economic corrosion is readily explainable.

The principal factors on which this new ability to test is based, are:

1. The completion of the electrochemical considerations connected with corrosion by knowledge of the effect of cells (concentration cells) caused by differences in the electrolyte[3,4] as well as by differences in electrodes.

2. The widespread effect of oxidizing agents, especially oxygen[5,6] of the air in solution, even in corrosion by strong acids and other electrolytes.

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[2] J. F. Thompson: *Op. cit.*

[3] R. J. McKay: Corrosion by Electrolyte Concentration Cells. (Abst.) *Trans.* Am. Electrochem. Soc. (1922) **41,** 201.

[4] R. J. McKay: The Common Occurrence of Corrosion by Electrolyte Concentration Cells. *Ind. & Eng. Chem.* (1925) **17,** 23.

[5] J. F. Thompson and R. J. McKay: The Control of Motion and Aeration in Corrosion Tests. *Ind. & Eng. Chem.* (1923) **15,** 1114.

[6] O. B. J. Fraser, D. E. Ackerman and J. W. Sands: Controllable Variables in the Quantitative Study of the Submerged Corrosion of Metals. *Ind. & Eng. Chem.* (1927) **19,** 332.

3. The varying types of films[7,8] formed during corrosion; their protective and accelerative effect.

4. The controlling effect of motion[9,10] in the solution, by its effect in producing or effacing concentration cells, removing films, and supplying oxygen and other corrodents to the corroding surface.

The control of the above factors as well as those of older recognition, temperature and acidity, puts laboratory corrosion testing on a fairly sound basis. But the recognition of some of these factors is so new that it is still inadvisable to design on the basis of laboratory tests alone. Wherever possible, laboratory tests should be paralleled by service tests. The laboratory should be acquainted with the service conditions so it may judge the possibility of service variations in the important factors. The service tests should be made with full knowledge of the current laboratory results which illustrate the relative importance of the varying factors in the corrosive media and metals under study. The conclusions drawn from each will always be modified by results from the other and the results of both should be a close approximation to the truth.

Obviously this is a slow and laborious method. The large number of tests described in the present paper illustrates this. But we are still unable to make accurate corrosion tests on a large scale. The only places where a series of tests made rapidly on a large range of alloys or corrosion conditions is of much value are such special ones as the determination of the best of a range of possible alloys for one specific purpose. In the preparation of a general reference work on corrosion-resisting alloys the author has consulted many thousands of what might be called "individual" results from "wholesale" tests and from them no practical conclusions can be drawn. A true corrosion test must still be made by the laborious method illustrated herein.

Corrosive Medium

Milk is seldom selected by metallurgists as a corrosive medium, therefore its selection in this case may deserve comment. Next to natural water, milk is the liquid which is produced or handled in the greatest quantities in the United States. To illustrate this the following comparison is given with the best known and largest quantity chemical liquid, sulfuric acid. In 1925, the last year for which figures are available, the production in the United States in terms of 50° Bé. sulfuric acid and whole milk was:

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[7] U. R. Evans: Corrosion of Metals, 2nd ed. London, 1926. Ed. Arnold & Co.

[8] W. H. J. Vernon: Second Experimental Report to the Atmospheric Corrosion Research Com. (British Non-ferrous Metals Research Assn.). *Trans.* Faraday Soc. (1927) **23**, 113.

[9] Thompson and McKay: *Op. cit.*

[10] Fraser, Ackerman and Sands: *Op. cit.*

	Tons
Sulfuric acid	7,000,000
Whole milk	58,000,000

The production is eight times as great as that of its nearest rival. In addition there is no liquid whose handling requires greater refinement of apparatus. It is stated that the dairy industry represents the greatest money value of any single commodity industry.

The chemical composition of milk is treated elsewhere. It is enough to point out here that it is an active chemical mixture of extreme interest from its corrosion reactions. In its handling the use of nonmetallic materials as well as metals has been considered, and the use of metals can continue only if their properties fully justify it.

Corroded Metals

During the last few years the dairy industry has undergone wide engineering advances in the handling of the product. One of the studies which the engineers of the industry have had constantly before them has been the best material, metal or otherwise, for contact with the product. At the present time solid nickel tanks and tubing are the greatest rivals of the older and cheaper types of construction, although other alloys are under laboratory and field test and nonmetallic materials have certain inherent advantages. Monel metal was considered for a time as the most logical metal for wide use, but, as a result of the corrosion tests and other considerations herein described, has been relegated to a few special uses.

Only enough tests have been included to illustrate the method or plan used. Such boundary tests as those on other metals, brines, waters, and cleaners, jointing materials and electrolytic effect of various seam types, and many tests on taste and toxicity have been omitted for the sake of brevity.

Part I.—Laboratory Studies

By O. B. J. Fraser

When it became evident that machinery and equipment for the dairy industries represented an important field of usefulness for pure nickel, and possibly for some of its alloys, a program of research was undertaken in order to determine if nickel was appreciably soluble in milk, and if dissolved nickel would have any undesirable effects upon it. The research was conducted for the most part at the Mellon Institute of Industrial Research, Pittsburgh, Pa., and more recently at the research laboratory of the International Nickel Co. at Bayonne, N. J.

The basic raw material of the dairy industries is cow's milk, which, like most materials of biological origin, is a heterogeneous mixture of

great complexity. It is subject to profound chemical alteration as the result of fermentative action induced by bacteria preexisting in it, or added to it in the manufacture of common buttermilk, acidophilus milk, the various types of cheese, etc. The induced alteration includes usually the conversion of lactose, or milk sugar, into lactic acid as the principal reaction. Other, and frequently undesirable, fermentative or oxidative changes may occur as the result of bacterial or enzymic action.

At first thought it might appear that a study of the action of lactic acid solutions on metals and alloys would serve as a basis for comparisons. The problem is by no means so simple, for some of the other components of milk either act upon metals or exert a marked inhibitory influence on the action of the lactic acid present.

Summary

It has been found experimentally, and confirmed by the work of others, that minute amounts of nickel are dissolved by sweet milk, sour milk or buttermilk. The amounts are much too small to be of any influence on the consumers of dairy products, and the quality of the products is not affected injuriously. Monel metal is somewhat less soluble than nickel. The experimental results indicate a possible maximum absorption in commercial pasteurization and storage of sweet milk in nickel equipment of 12 p.p.m. This is a small amount and considerably greater than actually has been found either in sweet milk or in buttermilk which has been processed almost entirely in nickel apparatus.

Agitation increases the solubility of nickel in milk at storage and at pasteurizing temperatures, where the acidity is practically constant, but has no appreciable effect at room temperature, where the acidity increases during tests.

The solubility of nickel is much greater with increased aeration in buttermilk at low temperatures, and in sweet milk and buttermilk at elevated temperatures, but it is less in sweet milk at low temperature.

Temperature has little influence on the solubility of nickel in sweet milk within the storage and room temperature ranges, but at higher temperatures, and especially with aeration, the solubility is much greater. Nickel dissolves more rapidly at higher temperatures in aerated buttermilk, but there is practically no increase without aeration.

Acidity affects the solubility of nickel in a variable manner dependent upon aeration and temperature. With insufficient aeration the solubility is lower in milk of higher acid concentrations, but the reverse is true with increased air supply. In the latter case the influence of acidity is relatively greater at low than at high temperatures.

Dark films form sometimes on the surfaces of nickel and monel metal in milk. These are composed largely of milk proteins, the color being

due to a small content of metal sulfide. The amount of tarnish varies with the rate of metal solution; with the lower rates dark colored films are not formed. The films are not completely protective, and they can be removed readily by abrasive cleaners.

At lower temperatures the solubility of both materials is greater in winter than in summer milk, but there is no seasonal difference at the pasteurizing temperature.

The solubility of both materials in pure lactic acid solutions is much greater than in milk of equivalent acidity, under the same conditions. The solubility of nickel in lactic acid solutions is lowered slightly by additions of casein and very greatly by milk albumen. That of monel metal is lowered greatly by these two milk proteins and by butterfat. The effects of albumen and butterfat are additive. Lactose also decreases the solubility of both materials slightly.

Egg albumen and gelatin solutions, with no added acid, dissolve nickel and monel metal to an appreciable extent, and at the same time produce upon them black and brown tarnishes, respectively. Solubilities of both materials in solutions of lactose, blood albumen or casein are very low, about the same as in distilled water.

Influence of Metals on Quality of Dairy Products

As a necessary part of the "corrosion" problem involved in the action of any food substance on the materials of the equipment in which it may be processed or stored, consideration must be given to the influence of absorbed metals on the quality of the product, and also to possible effects on the ultimate consumers of the product.

There were several articles dealing with certain of the aspects of interactions between milk and metals in the literature at the time experimental work was begun, but none of them contained quantitative information on the rate of solution of metals in milk. These and later articles, some of which did contain solubility data, are listed in the bibliography at the end of Part I.

Several of the articles listed contain definite evidence that even very small amounts of dissolved metals may exert great influence upon the keeping quality of dairy products. Iron and copper catalyze certain oxidative changes which result in the development of off-flavor or spoilage in milk or in products made from it. Because of this possibility monel metal, as it is a nickel-copper alloy, is considered to be less desirable than nickel for dairy equipment despite the fact that nickel is somewhat the more soluble in milk.

Several authors,[9,21,34,35][11] have stated that nickel has no influence upon the flavor or keeping qualities of milk or milk products, though one

[11] Numbers in parenthesis refer to bibliography at end of Part I.

of them[35] did report from laboratory tests the detection of a very slight change in flavor of milk in contact with nickel. However, his experience with nickel apparatus on a commercial scale did not check the laboratory results. No changes in quality were observable in the commercially processed products.

Neither nickel nor monel metal affected the flavor of milk injuriously in tests conducted by the author and various associates. These tests were carried out in the laboratory by submerging pieces of metal for periods of 18 to 20 hr. in unpasteurized, sweet milk contained in stoppered bottles. Tests were made at 5° C. and at room temperature. There were scarcely any increases in acidity during the tests at 5° C., but at room temperature final concentrations as high as 0.5 per cent. were recorded. Similar results were obtained by Searle[26] in tests conducted in milk freshly drawn from the cow into a sterile glass container, and also in partially evaporated milk and in remade milk from milk powders.

A peculiar case in which brief contact with monel metal seemed to accelerate a preexisting tendency toward development of an oily flavor in milk is discussed in the second part of this paper.

Influence of Metals on the Human Organism

The influence of metals on the human or animal organism depends not only on the quantity of metal taken in, but also on the manner in which it enters the body and particularly on the chemical nature of the metal-containing substances. Simple salts of the heavy metals in quantity may be corrosive to the walls of the gastro-intestinal tract, but minute amounts of metals ingested in foods do not enter the body in such corrosive combinations. Instead they form practically insoluble compounds with protein constituents of the food materials, and for the most part are excreted rapidly.

Nickel is an element which is distributed very widely in soils and plants[41,42] and it is ingested normally in food products throughout the world. Its physiological and metabolic significance have been studied by several investigators[36–41], who have concluded that it exerts no harmful effects. Offerdahl[38] consumed 500 mg. of powdered nickel in his food daily for one month with no noticeable effects. Other investigators[36,37,40] observed over periods of time extending into years the physical behavior of groups of people living upon food cooked only in nickel utensils. There were no noticeable disturbances of body functions.

As is noted in Part II of this paper, market milk pasteurized in a plant in which almost every piece of equipment and all the service piping were of nickel, absorbed only 1.3 p.p.m. of nickel. Buttermilk, which had been processed in a nickel vat, contained 1.4 p.p.m. of nickel. The highest figure for nickel absorption noted in commercial practice has been 15.7 p.p.m., in acidophilus milk, which is a product containing as high

as 1.2 per cent. lactic acid. It is interesting to note that calculations[26] from the laboratory experiments described in this paper indicated that there might possibly be a maximum of 12 p.p.m. of nickel, or 5.5 p.p.m. of monel metal dissolved in sweet milk during pasteurization and storage in nickel equipment. Other investigators[23,43] have estimated, also from laboratory test data, that during the pasteurization period only, the amount of metal which might be absorbed from nickel apparatus would be of the order of 0.29 to 1.23 p.p.m. These figures represent very small and unimportant quantities of metal from the health standpoint, as may be judged from the facts that the legal limit for copper in foods in this country is 30 p.p.m., and that there is no legal limit at all for nickel. The maximum figure quoted for nickel in a dairy product, namely 15.7 p.p.m. in acidophilus milk, corresponds to 61 mg. per gallon of milk.

Laboratory Corrosion Testing Procedure

Pasteurizing vats appeared to be the most important machines for consideration at the time experimental work was begun, so the laboratory procedure was designed to simulate the conditions of service of such equipment.

In vat pasteurization, which is a "batch" process, sweet milk is heated usually to 61° to 63° C. (142° to 145° F.), and held at that temperature for 30 min., after which it is cooled to 4.5° to 7° C. (40° to 45° F.), and either held in the pasteurizer or passed along to a larger storage tank. Fermented or "ripened" milk products, such as buttermilk, butter starter, etc., are also made in pasteurizing vats.

During the pasteurizing and cooling periods the milk is kept in constant, but not violent, motion by a helical coil revolving at low speed. Hot or cold water may be passed through the coil at will. The vats are covered during the processing period, and the air space above the milk is usually small, so that a condition of limited aeration exists, with a gentle movement of the milk past the metal surfaces.

Tests were run at about 10° C. (50° F.), at room temperature, and at 63° C. (145° F.). There was free development of lactic acid in the tests at room temperature, which were run for periods of 17 or 18 hr., so that they were roughly representative of the ripening process employed in buttermilk manufacture. Tests at 10° C. or lower, which were run in a cold room in which the temperature varied between 3° and 10° C., were representative of the conditions maintained during the storage of sweet milk. Those at 63° C., in which the bottles containing the milk were immersed in a thermostatically controlled water bath, were considered to be representative of pasteurizing conditions, though they were run for 4 hr. in the same bath of milk, whereas the usual pasteurizing time is only 30 min. at full temperature plus the time consumed in heating the milk from, and cooling it to the holding temperature. Quam,

Soloman and Hellwig[33] have suggested that it would be better in laboratory corrosion testing to make repeated exposures of 30 min. each in fresh samples of milk, rather than to use a single sample for a long period of time. In support of this opinion they cite the work of Whittier and Benton[44], who found that milk undergoes chemical alteration when held at 95° C. to boiling temperature for periods up to 14 or 16 hr. The principal change is in hydrogen-ion concentration, which increases continuously until the casein begins to precipitate, at which time there is a sharp decrease.

The milk was not aerated in any of the tests, and the temperature was not controlled closely in tests at room or lower temperature. The failure to control the temperature closely in the lower temperature tests, and the aeration in all tests might be open to criticism were it not that service conditions were thereby more closely approximated, and that the nature of the action of milk on metals makes it unnecessary to exercise such close control as is generally desirable in corrosion studies. The results obtained served their purpose very well, though, as is shown in Part II, they did not permit accurate prediction of the probable behavior of the metals in all types of dairy apparatus.

Solubilities of Nickel and Monel Metal

The method of weight-loss determinations was employed because, at the time, no satisfactory analytical methods were available for the determination of small amounts of nickel in biological materials.

All of the earlier work is summarized in Tables 1 and 2. The test pieces used were of sheet metal, 0.079 by 2.5 by 6 cm., having a total surface area of approximately 0.3 sq. dm. These were cleaned before each test by rubbing with No. 0 metallographic emery paper, followed by washing with water and rinsing with alcohol-ether mixture. After each test the pieces were again washed, rinsed in alcohol-ether mixture, and dried before weighing. The milk was obtained in the unpasteurized condition from a large Pittsburgh dairy. A volume of 500 c.c. was used for each test piece, this volume bearing the same relation to the area of a test piece as the volume of milk in a 700-gal., horizontal, coil type pasteurizing vat bears to the submerged metal surface therein.

Each test piece was totally submerged in a separate bath contained in a 1000-c.c. tall form, wide-mouthed bottle. The test piece was suspended from a wire across the mouth of the bottle, and the milk was kept in constant motion by a glass stirrer, operated by a motor-driven, multiple-spindle stirring apparatus. The moderate agitation thus obtained was reasonably similar in form to that occurring in a pasteurizing vat, and the aeration was limited because of the large volume and depth of the still air in the bottle above the milk.

As a matter of convenience in discussion, temperatures will be referred to three ranges. "Storage temperature" will imply temperatures between 2° and 11° C. (36° and 52° F.); "room temperature" between 18° and 28° C. (64° and 82° F.), and "pasteurizing temperature" between 60° and 65° C. (140° and 149° F.). Reference to the various tables will serve to disclose the actual values in each case. The letters "mdd." will be used throughout the discussion of corrosion rates as an abbreviation of "mg. per sq. dm. per day".

The data of Table 1 show very large variations among corrosion rate determinations obtained under similar conditions. The reason lies

TABLE 1.—*Weight-loss Tests in Unpasteurized,*[1] *Pittsburgh Milk, with No Artificial Aeration*

Volume of milk in each test, 500 c.c. Test piece area, 0.3 sq. dm.

Time of tests, 4 hr. at 63° C.; 17 to 18 hr. for most tests at other temperatures, with a few at 12 to 23 hours.

Temperature		Acid, as Lactic, Per Cent.		Nickel				Monel Metal			
				Number of Tests	Loss, Mg. per Dm.[2] per Day			Number of Tests	Loss, Mg. per Dm.[2] per Day		
Deg. C.	Deg. F.	Initial	Final		Maximum	Minimum	Average		Maximum	Minimum	Average
Summer Milk, Quiet Tests											
23 to 27	73 to 81	0.159	0.836	18	11.8	2.29	6.60	26	11.48	+1.52	2.37
Summer Milk, Agitated Tests											
3 to 11	37 to 52	0.172	0.230	7	6.9	0.89	2.96	9	2.1	0.0	1.01
23 to 27	73 to 81	0.147[3]	0.638[3]	20	26.7	1.30	8.70	6	5.79	0.46	2.24
63	145	0.138[3]		9	413.0	202.0	287.0	5	206.0	179.0	194.0
Winter Milk, Quiet Tests											
23 to 27	73 to 81							1[6]			2.18
Winter Milk, Agitated Tests											
3 to 11	37 to 52	0.134	0.137	7	61.3	0.0	17.0	5	13.5	8.32	10.4
23 to 27	73 to 81	0.139[4]	0.492[5]	24	37.0	2.12	12.44	20	30.7	2.59	16.22
63	145	0.132[3]		6	334.0	162.0	267.0	5	248.0	143.0	190.0

[1] Pasteurized milk used for 6 nickel and 14 monel determinations in summer milk, quiet tests.
[2] Acidity not determined for 3 nickel and 3 monel tests.
[3] Acidity determined only at start of tests.
[4] Acidity not determined for 2 nickel and 1 monel test.
[5] Acidity not determined for 1 nickel test.
[6] Acidity not determined.
+ indicates a gain in weight.

TABLE 2.—*Lactic Acid Determinations to Accompany Table* 1

Nature of Tests	Acidity, Per Cent.		
	Maximum	Minimum	Average
Quiet, summer, 23 to 27° C., initial:			
Pasteurized	0.187	0.108	0.136
Raw	0.196	0.159	0.178
All			0.159
Quiet, summer, 23 to 27° C., final:			
Pasteurized	0.866	0.620	0.780
Raw	0.970	0.832	0.881
All			0.836
Agitated, summer, 3 to 11° C., initial	0.200	0.155	0.172
Final	0.250	0.200	0.230
Agitated, summer, 23 to 27° C., initial	0.195	0.125	0.147
Final	0.809	0.425	0.638
Agitated, summer, 63° C., initial	0.145	0.130	0.138
Agitated, winter, 3 to 11° C., initial	0.146	0.115	0.134
Final	0.174	0.115	0.137
Agitated, winter, 23 to 27° C., initial	0.153	0.120	0.139
Final	0.690	0.170	0.492
Agitated, winter, 63° C., initial	0.150	0.120	0.132

TABLE 3.—*Weight-loss Tests on Nickel and Monel Metal in Summer Milk at* 20 *to* 26° *C.* (68° *to* 79° *F.*)

[Test Pieces Were Not Resurfaced between Successive Tests]

Test	Acid, as Lactic, Per Cent.		Loss, Mg. per Dm.² per Day					
			Nickel			Monel		
	Initial	Final	Piece *A*	Piece *B*	Average	Piece *A*	Piece *B*	Average
1	0.125	0.665	1.9	1.4	1.65	0.00	0.33	0.17
2	0.135	0.694	3.4	2.1	2.75	0.32	0.65	0.49
3	0.130	0.708	3.1	2.1	2.6	0.95	0.98	0.97
4	0.130	0.705	2.2	1.7	1.95	0.32	0.65	0.49
5	0.130	0.685	3.4	2.1	2.75	0.32	0.00	0.16
6	0.150	0.605	3.3	3.7	3.5	0.42	0.87	0.65
7	0.120	0.570	4.1	2.3	3.2	1.7	3.1	2.4
8	0.125	0.523	3.7	7.4	5.55	5.1	3.9	4.5
9	0.125	0.637	2.8	4.6	3.7	1.7	1.3	1.5
Average			3.1	3.04	3.07	1.20	1.31	1.26

Volume of baths, 500 c.c.
Test piece area, 0.3 sq. dm.
Duration of each test, 18 hours.

more in the variability of the milk and the irregular nature of surface films formed by milk constituents and solid products of corrosion than in the lack of precise control of temperature. Aeration probably was not uniform, though close control of this variable was not desirable, since the test procedure was planned to simulate practical conditions. Temperature differences within the ranges for storage and for room temperature tests probably had some influence, but, as is shown in the discussion of Tables 7 and 8, the effects of temperature in such limited ranges are overshadowed by other influences. In tests at the pasteurizing temperature, the temperature was controlled closely. It must be remembered also that with the low corrosion rates which were by far the more numerous in this work, the influence of experimental errors was large in view of the fact that the weight changes involved were frequently only a few tenths of a milligram in a total weight of about 10 g. Under the conditions of test a difference in weight of 0.1 mg. represented a difference in corrosion rate of 0.44 mdd.

Influence of Agitation

The influence of agitation on the solubility of nickel was great at storage and pasteurizing temperatures, but unimportant at room temperature. This is apparent from Tables 1 and 4. In unaerated summer sweet milk at 2° to 4° C. (Table 4), the solubility of moving test pieces was 13 times that of still pieces. At pasteurizing temperature the solubility of moving pieces was 16 times that of still pieces. Similar results were obtained in buttermilk. At room temperature (Table 1), stirring of the ripening milk had no appreciable effect on the solubility of either nickel or monel metal.

Agitation of the types employed in these tests probably represented closely enough that occurring in a pasteurizing or storage vat, but the very large acceleration due to the extremely rapid movement of milk over a surface cooler, under conditions suitable for maximum aeration could not have been predicted from the results obtained. The field tests described in Part II were essential for a proper understanding of the corrosion problem involved in surface coolers.

Influence of Aeration

The influence of aeration on the solubility of nickel in milk is very great. It is shown markedly in the figures of Table 4, and also in field tests discussed in Part II. Corresponding data for monel metal were not sought.

The data of Table 4 were obtained in tests run at Bayonne, N. J. Test pieces were 0.079 by 3 by 5 cm., and they were prepared and handled in exactly the same manner as has already been described for the Pittsburgh tests. The volumes of milk used were 2000 c.c. for unaerated,

TABLE 4.—*Weight-loss Tests on Nickel in Bayonne Summer Milk, Showing Influence of Aeration, Acidity, Temperature and Velocity*

Solution	Temperature		Linear Speed,[1] Ft. per Min.	Acid as Lactic, Per Cent		Conditions of Aeration	Number of Tests	Loss, Mg. per Dm.[2] Day		
	Deg. C.	Deg. F.		Initial	Final			Maximum	Minimum	Average
Sweet milk, pasteurized	2 to 4[3]	36 to 39	19[5]	0.148 to 0.154	0.148 to 0.163	Unaerated.	8	109.0	1.8	55.9
Sweet milk, pasteurized	2 to 4[3]	36 to 39	19[5]	0.148 to 0.154	0.148 to 0.163	Aerated.	4	18.1	2.2	6.5
Sweet milk, pasteurized	2 to 4	36 to 39	150			Air-free.	1			+0.6
Sweet milk, pasteurized	4	39	None	0.154	0.163	Unaerated.	1			4.2
Sweet milk, pasteurized	4	39	None	0.154	0.163	Unaerated, waterline test.[6]	1			41.5
Sweet milk, unpasteurized[2]	25[4]	77[4]	None	0.163 to 0.166	0.166 to 0.170	Unaerated.	4	13.6	7.0	10.3
Sweet milk, pasteurized	63 to 64	145 to 147	19[5]	0.145 to 0.236		Unaerated.	8	142.0	41.0	97.9
Sweet milk, pasteurized	61.5 to 63	143 to 145	19[5]	0.145 to 0.236		Aerated.	4	493.0	251.0	376.0
Sweet milk, pasteurized	63	145	None	0.167 to 0.236		Unaerated.	2	7.6	4.7	6.1
Sweet milk, pasteurized	63	145	None	0.236		Unaerated, waterline test.[6]	1			49.1
Buttermilk	2 to 4	36 to 39	19[5]	0.770 to 0.970	0.770 to 0.954	Unaerated.	8	140.0	11.0	46.8
Buttermilk	2 to 4	36 to 39	19[5]	0.770 to 0.970	0.770 to 0.954	Aerated.	4	272.0	226.0	250.0
Buttermilk	2 to 4	36 to 39	150			Air-free	1			1.1
Buttermilk	2 to 4	36 to 39	150			Gassed with commercial nitrogen.	1			1.1
Buttermilk	2 to 4	36 to 39	None			Unaerated.	2	2.7	1.5	2.1
Buttermilk	4	39	None	0.970		Unaerated, waterline test.[6]	1			14.6
Buttermilk	20	68	19			Unaerated.	1			4.2
Whey	20	68	19			Gassed with commercial nitrogen.	1			12.5
Sweet milk[2] plus pure lactic acid	25[4]	77[4]	None	1.000	1.004	Unaerated.	2	7.18	4.77	5.97
Buttermilk	63 to 64	145 to 147	19[5]	0.630 to 0.840	0.630 to 0.850	Unaerated.	7	89.0	23.6	50.7
Buttermilk	63 to 64	145 to 147	19[5]	0.630 to 0.840	0.630 to 0.850	Aerated.	4	608.0	352.0	502.0
Buttermilk	63	145	None	0.84 to 0.93	0.85 to 0.90	Unaerated.	2	3.75	+4.35	+0.3
Buttermilk	63	145	None	0.84	0.85	Unaerated, waterline test.[6]	1			64.3

[1] Rate of travel of test pieces through solution; those at 19 ft. per min. revolving in a vertical orbit, those at 150 ft. per min. in a horizontal orbit.
[2] A group of tests run in winter (March) milk.
[3] Starting temperature for 2 unaerated and 1 aerated tests was 7.5° C., falling to 4° C. in 3.5 hours.
[4] Approximate temperature; not controlled.
[5] One test run at 15.5 ft. per min.
[6] Test piece only partially submerged; weight-loss calculated on submerged area.
+ Indicates a gain in weight.
Volume of baths: 2000 c.c. in unaerated tests, 4000 c.c. in aerated tests, 4500 c.c. in air-free and nitrogen-saturated tests.
Area of test pieces: 0.3 sq. dm., except for tests referred to in footnote 2, in which the area was approximately 0.75 sq. dm.
Duration of tests; 4 hr. at temperatures of 61.5° C. and higher; 20 hr. in all other tests.

4000 c.c. for aerated and 4500 c.c. for air-free and nitrogen-saturated tests. Using two pieces, of the dimensions given above, in each bath, a total metal surface of approximately 0.6 sq. dm., the volumes of milk per sq. dm. of metal surface were 3300 c.c., 6600 c.c. and 7500 c.c., respectively, as against 1667 c.c. per sq. dm. in the Pittsburgh tests. Unaerated and aerated tests were run in a circular-path apparatus, and air-free and nitrogen-saturated tests in a rotating-spindle apparatus, both of which have been described by Fraser, Ackerman and Sands.[47]

In the unaerated tests the surface of the milk was exposed freely to the atmosphere. In the aerated tests air was bubbled into the milk at the bottom of the containers (battery jars) through open glass tubes. In the air-free tests the closed vessel in which they were run was filled completely with milk. A similar condition was maintained in the nitrogen-saturated tests.

In sweet milk at 2° to 4° C., the solubility was 8.5 times as great without as with aeration, but a small gain in weight was found in a single test in air-free milk. At 63° C., however, aeration increased the solubility 4 times.

Aeration increased the solubility at both temperatures in buttermilk, 5 times at 2° to 4° C., and 10 times at 63° C. In nitrogen-saturated and air-free buttermilk the solubility at 2° to 4° C. was only a little more than 2 per cent. of that in the unaerated buttermilk. At 20° C. a single test in each case indicated that the solubility was greater in nitrogen-saturated than in unaerated buttermilk.

The larger corrosion rates in aerated milk, especially in buttermilk, were accompanied by visible etching of the metal surface.

The influence of aeration is indicated also by the greater solubility in both sweet milk and buttermilk, and at both low and high temperatures, of test pieces which were submerged only partially in unagitated baths. The partially submerged pieces had solution rates from 7 to 17 times those of totally submerged pieces. There was, however, no visible "waterline" corrosion, simply a narrow band of darker brown than the general tarnish on each test piece.

In all of these tests the tarnish was most apparent at the pasteurizing temperature, and particularly in aerated milk. The maximum effect was obtained in aerated buttermilk.

Influence of Temperature

Temperature over a wide range has a very great effect, as may be seen on comparing, in Table 1, the rates at 3° to 7° C. with those at 63° C., for nickel and monel metal in agitated tests. (The data of Table 1, for winter milk, are plotted in Fig. 1.) The rates for nickel in winter milk were 17.0, 12.44 and 267.0 mdd. at storage, room and pasteurizing temperatures, respectively. The corresponding rates for

monel metal were 10.4, 16.22 and 190.0 mdd., respectively. The reversal of the relative positions of the two materials at room temperature is due possibly to some specific effect upon the mechanism of corrosion which comes into play as the acidity increases. The increase in acidity during the test period was much less in winter than in summer milk. The same influence of temperature in increasing the rates of solution is shown for summer sweet milk in the data of Table 4, for tests run with nickel at Bayonne. In sweet milk the corrosion rate in unaerated tests with moving test pieces was 56 mdd. at 2° to 4° C. while it was 98 mdd. at 64° C. In buttermilk the rate was 47 mdd. at 2° to 4° C., while it

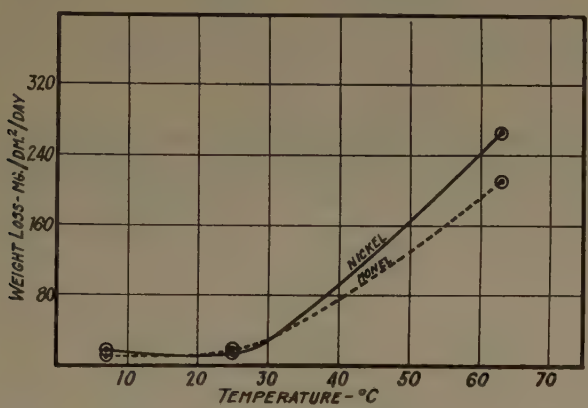

FIG. 1.—INFLUENCE OF TEMPERATURE ON RATE OF SOLUTION OF NICKEL AND MONEL METAL IN AGITATED, WINTER MILK.

was only 51 mdd. at 64° C. With aeration, buttermilk came into line, the rates being 250 mdd. at 2° to 4° C. and 502 mdd. at 64° C. Monel metal was not included in the Bayonne tests.

Influence of Acid Concentration

The influence of acidity (see Table 4) depended very much on conditions of aeration and temperature. In aerated tests the solubility of nickel was greater in high-acid buttermilk than in low-acid sweet milk by 38 times at 2° to 4° C., but by only 1.3 times at 64° C. In unaerated tests the solubility was greater in the low-acid sweet milk. The ratios of buttermilk as to sweet milk solution rates were 0.8 at 2° to 4° C., and 0.5 at 64° C.

At the pasteurizing temperature the buttermilk tests were actually tests in whey only, for the proteins coagulated at once and settled to the bottom of the vessel. The whey was considerably lower in acid concentration than the original buttermilk, indicating a large fixation of acid by the coagulated protein. The original buttermilk had acidities of 0.896 to 0.932 per cent., but those of the whey were only 0.630 to

TABLE 5.—*Weight-loss Tests on Nickel in Unagitated Sweet Winter Milk, with No Movement of Test Pieces*

[Temperature 60° C. (140° F.); Volume of Baths, 350 c.c.]

Duration, Hr.	No. of Tests	Acid, as Lactic, Per Cent.		Area, Sq. Dm.	Loss, Mg. per Dm.² per Day	
		Initial	Final		Total	Per Day
20	2	0.168 to 0.180	0.236 to 0.384	1.0	11.5	13.8
20	2	0.17 to 0.19	0.36 to 0.40	0.5	7.35	8.82
Average					9.43	11.31
7	1	0.180	0.222	1.0	8.2	28.0
5	1	0.168	0.212	1.0	12.6	60.5

TABLE 6.—*Weight Loss Tests on Nickel and Monel Metal in Sweet Milk, Sour Milk and Pure Lactic Acid Solutions*[12]

Solution	Acid, as Lactic, Per Cent.	Loss, Mg. per Dm.² per Day			
		Nickel		Monel Metal	
		18° C. (64° F.)	65° C. (149° F.)	18° C. (64° F.)	65° C. (149° F.)
Sweet milk	0.2		7.5		5.0
Sour milk	0.26	0.95	9.5	0.45	6.5
Lactic acid	0.2	2.1	41.5	1.25	36.0

0.674 per cent. The observations of Whittier and Benton(44) on the sharp drop in hydrogen-ion concentration with the coagulation of the proteins in heated milk may be referred to again. One test of Table 4 was run in whey which had been separated completely from the coagulated curd and cooled to room temperature.

In some quiet, unaerated tests at room temperature the solubility of nickel was 10.3 mdd. in sweet milk against only 5.97 mdd. in the same milk to which pure lactic acid had been added to a total acidity of 1.0 per cent. These results are not included in Table 4.

The influences of acidity is shown also in Table 6, the data for which were taken from curves given by Donauer(23). Nickel and monel metal showed slightly greater solubility at 65° C. in milk of 0.26 per cent. acid than in milk of 0.20 per cent. acid. The difference in acidity was not great. The solution rates of both metals were much greater in 0.20 per cent. lactic acid solutions at both 18° and 65° C., than in milk of equivalent acidity.

[12] From graphs of Donauer: *Ice Cream Review* (1923) **5**, No. 6, 78–84.

Influence of Corrosion Products

Nickel and monel metal sometimes acquired a brown tarnish in milk, especially in buttermilk. The amount of tarnish, as measured by the depth of coloration, increased with the weight loss but, like the weight-loss figures, it was extremely variable. The tarnish was not usual at storage temperatures, but it did occur on occasions. Its nature was not determined precisely, but it was possible to get some rough analyses. The color was due apparently to a small content of nickel sulfide. The source of the sulfur was the protein portion of the milk, a small amount of which must have suffered partial splitting up in such manner that some of its constituent sulfur was in suitable combination for reaction with nickel as it dissolved. The action must have taken place rapidly, for nickel ions, like those of other heavy metals, react readily with proteins to form insoluble complexes. The remainder of the tarnish film undoubtedly was precipitated protein substance. In fact, in some of the tests in winter milk sufficient protein was precipitated on the metal to give a distinct, thin, smooth, white film on nickel, monel metal and some other metals and alloys. In view of the currently accepted theories of corrosion processes it is interesting to note that Robertson[46] found that, under the influence of a very small current, uncombined casein was deposited at the anode from a solution of potassium caseinate. It was found also, in the laboratory of the International Nickel Co., that the brown tarnish which would be formed normally under the test conditions employed could be prevented entirely by imposing upon nickel, as cathode, a current of small density, 0.0043 amp. per sq. dm. As anode, however, nickel lost in weight and was tarnished to a degree corresponding to the weight lost. It is inferred that some of the protein substance in milk migrates to the anodic spots on the metal surface and is there precipitated to form an even film which, in the case of nickel or alloys high in nickel, is colored sometimes by nickel sulfide. The reactions of the proteins by which sulfur is rendered available in proper form for the precipitation of nickel sulfide within the film possibly may be induced or accelerated by electrochemical oxidation.

That the films formed are permeable, though possibly somewhat protective, is demonstrated by the data of Table 3. Two pieces of nickel and two of monel metal were exposed at room temperature for 20 hr. on each of nine successive days, in summer milk fresh each day, under the same conditions as were imposed in the tests of Table 1, except that the tarnish film was not disturbed between tests. The pieces were simply rinsed in water, then in alcohol-ether mixture, then dried and weighed. The corrosion rates throughout were of the same order of magnitude as the corresponding rates in Table 1. The tarnish on nickel became increasingly darker with each succeeding immersion up to the

fifth, then it became slightly lighter in color. The tarnish on monel metal became increasingly darker up to the completion of the test.

These are not positive indications that the films may not become completely protective, for in this case they were dried out thoroughly between tests and given every opportunity to develop minute discontinuities at which fresh corrosion might begin. A little evidence in the other direction is afforded by the data of Table 5. These were quiet tests, with nickel only, conducted at 60° C. in sweet, winter milk. Tests run for 5, 7 and 20 hr. gave corrosion rates of 60.5, 28.0 and 11.31 mdd., respectively, but the total weights lost were 12.6, 8.2 and 9.43 mg. per sq. dm., respectively. The actual amounts of metal removed during each whole test period differed only slightly, which suggests that the tarnish film which had formed became protective so long as it was not altered by intermediate drying.

In a few of the tests summarized in Table 1 there were, as noted therein, actually slight gains in weight, which also suggests formation of a coherent film. It was deemed impracticable to remove the tarnish films at the time, and average values were arrived at by adding the weight changes algebraically and dividing by the total number of determinations.

Nature of Milk

It is recognized generally that there are seasonal variations in the chemical composition of milk, and probably there are variations also in the nature of contained bacteria and enzymes. The data of Tables 1 and 2 bring out striking seasonal differences in rates of metal solution and of lactic fermentation.

The solubility of both nickel and monel metal at storage and room temperatures was greater in winter than in summer milk, but the seasonal difference was not apparent at the pasteurizing temperature. A difference may also be noted in the rate of lactic fermentation. Both at storage and at room temperatures the amount of acid formed in the period of test was much less in winter milk than in summer milk. It must be noted, however, that the amount formed at room temperature was exceptionally low in a few of the tests in winter milk, largely because of unusually low temperatures during the night hours of the test periods. Also, from Table 2, it appears that previously pasteurized summer milk has a lower initial acidity and ripens a little more slowly at room temperature than unpasteurized milk. At all seasons of the year there are distinctly appreciable variations from day to day in the acidity of milk, and in the rate of lactic fermentation.

It is hardly profitable for metallurgists to speculate upon the probable reasons for seasonal variations in milk, or upon their nature. Biological chemists are not in agreement among themselves. The composition of milk is truly formidable. Wiley[45] has stated that milk contains water, proteins, fat, carbohydrates, organic and inorganic acids and mineral

salts. It may also contain minute amounts of ammonia, and many organic compounds other than those mentioned. Seligman[23] has quoted from a European authority a list of mineral salts occurring in milk, which comprises chlorides of sodium and potassium; phosphates of potassium, calcium and magnesium; citrates of potassium, calcium and magnesium; and lime combined with casein, in amounts ranging from 0.336 g. per l. dimagnesium phosphate to 2.133 g. per l. calcium citrate.

Roles of Various Milk Constituents

To learn something of the mechanism of the corrosion of metals in milk a number of tests were made, using methods similar to those

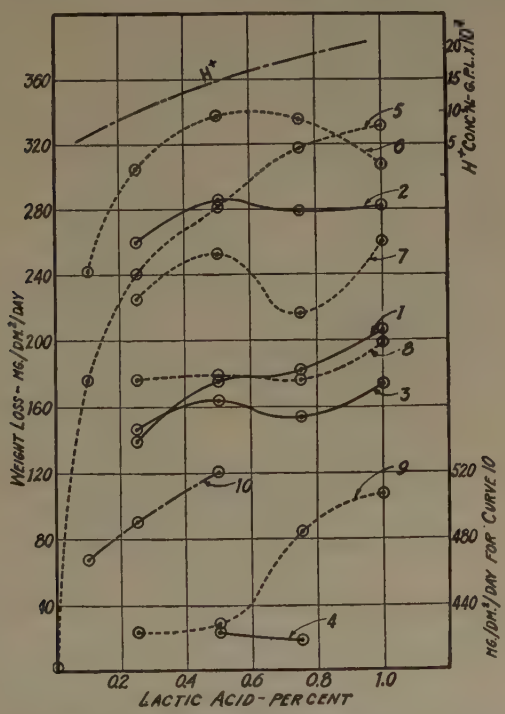

Fig. 2.—Influence of milk constituents on rate of solution of nickel in lactic acid solutions.

1, Acid only, at 6 to 11° C.; 2, acid plus cream at 6 to 11° C.; 3, acid plus butter at 6 to 11° C.; 4, acid plus butter and milk albumen at 6 to 11° C.; 5, acid only, at 18 to 28° C.; 6, acid plus cream at 18 to 28° C.; 7, acid plus butter at 18 to 28° C.; 8, acid plus casein at 18 to 28° C.; 9, acid plus milk albumen at 18 to 28° C.; 10, acid only, at 63° C.

described for the tests of Table 1, in aqueous solutions or emulsions of some of the organic constituents of milk and of some other substances of similar nature. The tests were conducted in the same manner as for the milk tests of Table 1. The sole differences were in bath composi-

tions. The results are contained in Tables 7, 8 and 9, and the curves of Figs. 2 and 3 were constructed from them. The hydrogen-ion curves were drawn from data contained in Van Nostrand's Chemical Annual. Unfortunately hydrogen-ion determinations were not made, either on these solutions or on any of the milk samples.

The fundamental solutions for Tables 7 and 8 were of pure lactic acid, containing from 0.1 to 1.0 per cent. thereof. In various tests there

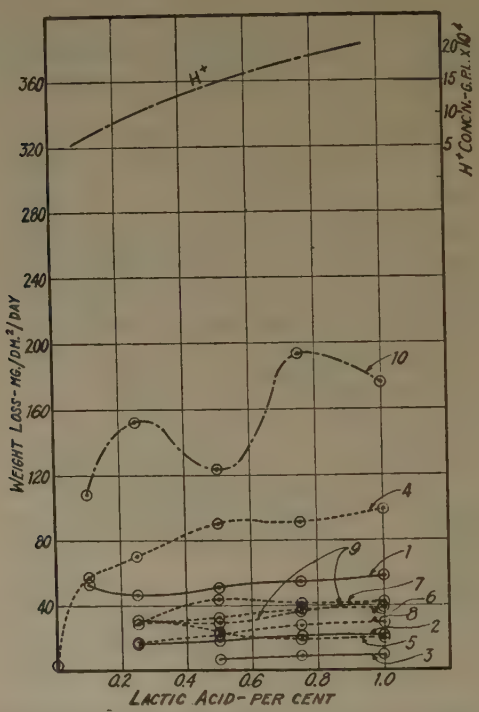

FIG. 3.—INFLUENCE OF MILK CONSTITUENTS ON RATE OF SOLUTION OF MONEL METAL IN LACTIC ACID SOLUTIONS.

1, Acid only, at 3 to 11° C.; 2, acid plus butter at 3 to 11° C.; 3, acid plus butter and milk albumen at 3 to 11° C.; 4, acid only, at 18 to 28° C.; 5, acid plus cream at 18 to 28° C.; 6, acid plus butter at 18 to 28° C.; 7, acid plus casein at 18 to 28° C.; 8, acid plus milk albumen at 18 to 28° C.; 9, acid plus butter, casein and milk albumen at 18 to 28° C.; 10, acid only, at 63° C.

were added to solutions of these acid concentrations one or more other milk constituents, in the proportions in which they usually occur in milk. The milk constituents used were butterfat, casein, milk albumen and milk sugar (lactose). In other tests soap, cottonseed oil, mineral oil or egg albumen were added to acid solutions. With butter and the oils there were added, as emulsifying agents, either saponin or saponin and gum acacia. Only a few tests were run at the pasteurizing temperature, and these were in pure lactic acid solutions only.

TABLE 7.—*Weight-loss Tests on Nickel in Aqueous Solutions of Lactic Acid, with and without Other Constituents of Milk*

Solution	Concentration Per Cent. by Weight	0.1 Per Cent. Acid				0.25 Per Cent. Acid				0.5 Per Cent. Acid				0.75 Per Cent. Acid				1.0 Per Cent. Acid			
		Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day		
			Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average
Temperature, 6° to 11° C. (43° to 52° F.); Duration, 18 Hours																					
Acid only						10	164	88	139	5	222	126	175	6	208	157	181	6	242	176	206
Acid plus butterfat[1]	3.75					4	292	223	259	6	319	224	285	4	309	248	278	4	324	244	282
Acid plus butterfat[2]	3.75					3	153	137	146	3	195	135	163	3	171	138	153	3	204	125	174
Acid plus butterfat[2] and milk albumen	3.75, 0.5[3]									1			23.4	1			18.7				
Temperature, 18° to 28° C. (64° to 82° F.); Duration, 18 Hours																					
Acid only		5	204	148	176	6	326	191	239	6	384	226	281	7	431	218	317	7	436	190	331
Acid plus butterfat[1]	3.75	5	308	185	241	5	332	277	305	4	372	309	337	5	388	244	335	8	395	238	307
Acid plus butterfat[2]	3.75					3	263	163	225	3	270	238	252	3	283	148	216	3	277	242	260
Acid plus lactose	4.5																	1			224
Acid plus casein	3.2					4	198	141	176	4	200	156	178	4	198	162	176	5	221	184	198
Acid plus milk albumen	0.5[3]					3	26.9	21.1	23.8	3	31.5	24.6	28.1	5	101	25.6	84	5	117	100	107
Acid plus butterfat and soap	3.75, 1.0																	1			76
Acid plus soap	1.0																	1			28.5
Acid plus cottonseed oil[4]	4.0																	1			105
Acid plus mineral oil[4]	4.0																	1			175
Acid plus egg albumen	0.5																	1			550
Temperature, 63° C. (145° F.); Duration, 4 Hr. in 0.1 Per Cent. Acid; 6 Hr. in Other Tests																					
Acid only		1			467	1			490	1			520								

[1] Added as sweet cream containing 25 to 27 per cent. of butterfat.
[2] Added as sweet butter; 0.1 per cent. of saponin also added as an emulsifying agent except in the test with soap and one test without any emulsifying agent.
[3] Total amount added; only about half of this went into solution.
[4] One-tenth per cent. of saponin and 0.2 per cent. of gum acacia added as emulsifying agents.
Volume of solution in each test, 500 c.c.; test piece area, 0.3 square decimeter.
Solutions stirred continuously but not aerated.

TABLE 8.—*Weight-loss Tests on Monel Metal in Aqueous Solutions of Lactic Acid, with and without Other Constituents of Milk*

Solution	Concentration Per Cent. by Weight	0.1 Per Cent. Acid				0.25 Per Cent. Acid				0.5 Per Cent. Acid				0.75 Per Cent. Acid				1.0 Per Cent. Acid			
		Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day			Number of Tests	Loss, Mg. per Dm.² per Day		
			Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average		Maximum	Minimum	Average
Temperature, 3 to 11° C. (37° to 52° F.). Duration, 18 Hours																					
Acid only		2	56.1	48.7	52.4	6	51.5	40.5	46.1	5	60.2	47.0	51.5	5	60.7	51.3	54.3	5	65.9	50.7	58.0
Acid plus butterfat[1]	3.75					3	16.8	15.2	15.8	3	18.6	18.0	18.3	3	20.3	20.0	20.2	3	22.8	19.9	21.0
Acid plus butterfat[1] and milk albumen	3.75, 0.5[3]									1			6.7	1			8.7	1			8.9
Temperature, 18° to 28° C. (64° to 82° F.). Duration, 18 Hours																					
Acid only		5	67.9	49.5	57.9	5	79.7	64.0	70.1	5	111.0	69.0	90.0	5	105.0	84.8	91.2	5	108.0	85.5	99.0
Acid plus butterfat[2]	3.2					3	34.9	23.8	31.3	3	34.2	27.0	29.9	2	36.3	30.2	33.3	2	31.5	25.4	28.5
Acid plus butterfat[2]	3.5					1			45.7	1			34.7	1			23.9	1			33.8
Acid plus butterfat[2]	3.75					7	40.2	15.4	28.5	7	29.3	5.63	19.4	6	21.2	4.40	13.7	9	30.8	5.30	16.9
Average[4]						11			30.8	11			23.7	9			19.2	12			20.2
Acid plus butterfat[1]	3.75					4	32.0	28.8	29.6	4	35.0	30.0	33.1	4	40.0	35.3	37.4	5	45.2	25.0	38.2
Acid plus lactose	4.5																	1			44.2
Acid plus casein	3.2					3	31.4	24.5	28.6	3	45.7	39.2	43.5	3	43.2	39.6	41.2	3	52.6	37.8	42.5
Acid plus milk albumen	0.5[3]					3	18.1	15.4	17.1	3	23.3	21.0	22.3	3	28.1	26.0	27.1	3	30.6	27.7	29.6
Acid plus butterfat[1] and casein and milk albumen	3.75, 3.2, 0.5[3]					3	35.4	19.1	30.5	3	35.5	17.2	29.3	3	41.0	34.0	36.4	3	48.5	39.3	42.6
Acid plus butterfat[1] and soap	3.75, 1.0																	1			24.5
Acid plus soap	1.0																	1			14.5
Acid plus cottonseed oil[5]	4.0																	1			48.7
Acid plus mineral oil[5]	4.0																	1			21.4
Acid plus egg albumen	0.5																	1			78.6
Temperature, 63° C. (145° F.). Duration, 4 Hr. in One Test in 0.25 Per Cent. Acid; 6 Hr. in Other Tests																					
Acid only		1			128.0	2	202.0	104.0	153.0	1			123.0	1			193.0	1			176.0

[1] Added as sweet butter; 0.1 per cent. of saponin also added as an emulsifying agent, except in the test with soap and one test without any emulsifying agent.
[2] Added as sweet cream containing 25 to 27 per cent. butterfat.
[3] Total amount added; only about half of this went into solution.
[4] Average of 3 sets of tests with butterfat added as sweet cream, in amounts from 3.2 to 3.75 per cent.
[5] 0.1 per cent. of saponin and 0.2 per cent. of gum acacia added as emulsifying agents.
Volume of solution in each test, 500 c.c.; test piece area, 0.3 square decimeter.
Solutions stirred continuously but not aerated.

TABLE 9.—*Weight-loss Tests in Aqueous Solutions of Some Milk Constituents and Other Proteins*

Solution	Concentration Per Cent. by Weight	Nickel				Monel Metal			
		Number of Tests	Loss, Mg. per Dm.[2] per Day			Number of Tests	Loss, Mg. per Dm.[2] per Day		
			Maximum	Minimum	Average		Maximum	Minimum	Average
Temperature, 8° C. (46° F.)									
Casein[1]	3.2	2	1.82	0.91	1.37	1			1.98
Egg albumen	0.6	2	35.5	26.4	30.95	1			58.9
Blood albumen	0.6	2	2.86	2.19	2.53	1			1.82
Gelatin	0.5	2	10.30	7.94	9.12	1			7.95
Temperature, 23° to 27° C. (73° to 81° F.)									
Casein[1]	3.2	5	5.2	+1.09	0.83	5	6.54	+2.63	0.89
Egg albumen	0.6	5	50.2	32.1	42.2	5	25.0	16.2	20.9
Blood albumen	0.6	5	5.51	+1.40	1.11	5	14.0	1.40	6.56
Gelatin	0.5	5	37.6	28.7	32.8	5	43.9	24.65	31.15
Lactose	4.5	5	5.1	0.96	2.91	5	4.55	0.56	2.32
Lactic acid	1.0[2]	5	314.0	126.0	267.0	5	115.0	62.4	83.8
Water, distilled		5	6.2	+0.48	2.43	5	4.38	0.56	3.14

[1] Dissolved in $Ca(OH)_2$ solution.
[2] In one test for each metal the acid concentration was 0.9 per cent.
+ indicates a gain in weight.
Volume of solution in each test, 500 c.c.; test piece area, 0.3 square decimeter.
Solutions stirred continuously, but not aerated.
Duration of tests, 17 to 18 hours.

Some difficulty was experienced in getting satisfactorily permanent emulsions of butter, and in getting some of the proteins dissolved. Milk albumen, although very finely ground, did not dissolve at all well. It was added to the extent of 0.5 per cent., but only about half of this dissolved. Butterfat added as sweet cream remained emulsified, but too much protein was added with the cream, hence sweet butter was used. In only one test was it possible to get a fairly permanent emulsion with the butter in the absence of assisting agents, but moderately good results were obtained with the addition of 0.1 per cent. of saponin.

Nickel exhibited a general tendency toward increasing solubility with increasing acid concentration, except in solutions containing sweet cream. Monel metal showed a corresponding tendency only in pure acid solutions. Sweet cream additions favored high rates of solution of nickel with the lower acid concentrations and particularly at low temperatures, but had little or no effect with the higher acid concentrations. Sweet butter had no effect on the solubility of nickel with low but reduced it considerably with high acid concentrations. Casein lowered

the solubility of nickel appreciably, and milk albumen reduced it to the same order of magnitude as in winter milk. Lactose caused a slight reduction. The solubility of monel metal was reduced by butterfat, casein, milk albumen and various combinations of these. The reduction with cream was somewhat greater than with sweet butter. Lactose also reduced the solubility of monel metal.

Egg albumen increased the solubility of nickel, but decreased that of monel metal. Cottonseed oil and mineral oil decreased the solubilities of both materials. Soap was decomposed, the resulting free fatty acid being deposited as a visible film on the metal surface, which it protected fairly well, as was shown by the large decreases in solubility of both materials.

The usual effect of temperature in increasing the solubility of metals and alloys was apparent.

In the lactic acid solutions, test pieces were etched lightly. In solutions containing butterfat, nickel sometimes showed a very faint tarnish, but monel metal was not changed in appearance. In all solutions containing both lactic acid and proteins, however, both metals were tarnished slightly.

Apparently the rates of solution of nickel and monel metal are lower in milk than in pure lactic acid solutions of equivalent acidity because of the inhibitory influence of the proteins, and, to some extent, of butterfat and lactose. The protective effect of butterfat is much greater on monel metal than on nickel. It is particularly noticeable that the effect of butterfat increases with increasing acid concentration, which may explain why the rates of solution of the metals are greater in winter milk than in the more acid summer milk.

The protein effect is probably twofold, partly the mechanical protection afforded by precipitated protein, and partly the fixation of hydrogen-ion, which reduces materially the effective acidity.

Butterfat acts probably in a purely physical manner, by coating the metal surface to some extent. Test pieces from tests with butterfat were slightly greasy to the touch. This explanation is supported by the similar effects produced by both cottonseed oil and mineral oil. It is also supported by the action of the soap.

The original data, which have been summarized in Tables 7 and 8, showed that the influence of temperature between 18° and 28° C., was negligible. Nickel in particular showed even lower solubility at 28° than at 21° C. The minor significance of temperature changes within the noted range for the room-temperature tests has been mentioned before in discussing the relative solubilities of nickel and monel metal in milk.

Table 9 contains the results of some tests conducted after the manner of those of Tables 7 and 8, in which nickel and monel metal were exposed

at storage and room temperatures to distilled water, and to solutions of lactic acid, lactose and several common proteins. Distilled water was the solvent for all except gelatin, for which limewater was used. The usual rates of solution were obtained in lactic acid solutions, and the solubilities were appreciable also in solutions of egg albumen and gelatin. In distilled water and the other solutions corrosion rates were very low, and of the same order of magnitude as in summer milk.

Both metals were tarnished heavily by egg albumen and gelatin solutions at room temperature, and by egg albumen at 8° C. At the lower temperature lighter tarnish films were produced. Blood albumen tarnished monel metal slightly at room temperature, but discolored only one piece of nickel, and that only faintly. Casein discolored monel metal very faintly at room temperature. Lactic acid solutions etched both nickel and monel metal at both temperatures but did not discolor either. No surface effects were apparent in other cases.

No study was made of the influence of the mineral salts which occur in milk. None of these are of themselves "corrosive" substances for either nickel or monel metal, and any effects which changes in concentration of these salts might exert on corrosion rates would be due probably to alteration of hydrogen-ion concentration through buffering action. The effect of changing hydrogen-ion concentration was covered by the tests in pure lactic acid solutions.

Acknowledgments

The author is indebted to numerous of his associates, past and present, for advice and assistance in the collection of the laboratory test data. He is particularly indebted to E. Ward Tillotson, J. W. Sands, D. E. Ackerman, and his coauthors of this paper.

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Part II.—Field Experiments

By H. E. Searle

Nickel dairy equipment gradually came into general use during the few years which followed the beginning of the investigations described in Part I. When nickel equipment became common and many different types were available for test, it was thought desirable to conduct field investigations to study certain matters of practical value to the designer and user of dairy equipment; such as the best methods of construction, the normal wear of equipment, the effect of nickel on milk, and the best cleaning methods.

Field Investigations in Pasteurizing Plants

The pasteurization of milk is the largest function of the dairy industry; consequently most attention was devoted to this branch.

The purpose of pasteurization is to destroy harmful bacteria which may be present in milk. Generally, it is accomplished by heating the milk to the thermal death point (142° to 145° F.) of the most resistant organisms and maintaining the temperature at that point until dangerous organisms are destroyed and the milk may be consumed with safety. The holding period is usually 30 min., after which the milk is cooled to about 40° F.

The apparatus used for pasteurizing milk varies in type and construction, depending largely on the quantity of milk to be handled each day. Small quantities of milk are handled in batches but large quantities are pasteurized in a continuous manner. A New York dairy pasteurizing large quantities of milk in typical equipment was selected for the field investigation of pasteurizing equipment.

Process and Equipment

The raw milk received at the plant was weighed and then passed through a filter, from which it was discharged either to a storage tank or directly to the pasteurizing equipment, according to operating conditions in the plant. The continuous pasteurizing plant consisted of a surface preheater, a multiple segment holding tank, a surface cooler, and the necessary pipe connections.

The surface cooler is illustrated in Fig. 4. It consists of a bank of 36 tubes, each of which is supported in a horizontal position. The bank is in a vertical position and the ends of the tubes are connected together in series. There are four groups, or sections, of eight tubes each, and one of four tubes. Either brine or cold water is circulated through the inside of the tubes in the small bottom section; the direction of flow is from bottom to top. Cold water is circulated through the inside of the tubes in the four top sections; the direction of flow is from bottom to top. Hot milk is received in the feed pipe at the top and flows through

a series of small holes, along the bottom of the pipe, onto the top tube of the surface cooler. The milk then flows downward by gravity, in a thin film, over the outside surface of each successive tube. The milk is cooled during its passage downward, the heat passing through the tube to the liquid within it. Upon leaving the bottom tube of the cooler, the milk is collected in the brine-jacketed collection trough below.

The surface heater is very similar in construction to the surface cooler. In its operation, hot water is circulated through the inside of the tubes; the direction of flow is from bottom to top. Cold milk is supplied to the

FIG. 4.—SURFACE COOLER USED FOR COOLING PASTEURIZED MILK.

feed pipe above, and hot milk is collected in the trough below. The flow of heat is from the hot water within the tubes to the cold milk flowing downward over their outer surfaces.

The multiple segment holding tank is illustrated in Fig. 5. It consists of a number of jacketed tanks each of which is shaped like the segment of a cylinder. The temperature of the milk in each tank is maintained within a narrow range by regulating the flow of hot water through the jacket. The whole apparatus is heavily insulated on the outside, to prevent loss of heat. Provision is made to rotate the tank slowly, and, by an ingenious arrangement, the milk is fed successively to each segment, in which it is held for 30 min. and then automatically dumped.

During the pasteurizing process, milk is fed continuously, for about 8 hr., to the surface preheater over which it flows and becomes heated to

about 143° F. It flows from the preheater to one of the segments in the holding tank in which it is held at 143° F. for 30 min., then it flows from the cooler to the bottling machines.

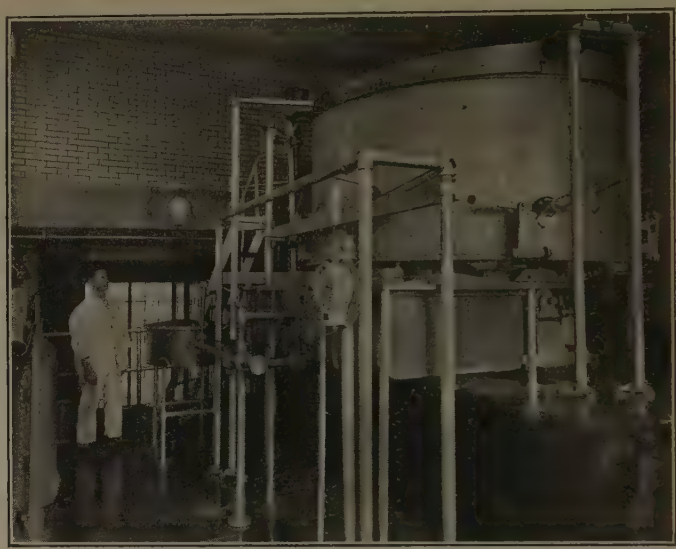


FIG. 5.—MULTIPLE-SEGMENT HOLDING TANK IN WHICH MILK IS MAINTAINED AT 143° F. FOR 30 MIN.

CORROSION TESTING AND METHODS OF TEST

In studying the influence of temperature, air, rate of flow, etc., on the corrosion of nickel and monel metal by milk, specimens were exposed at four points on the surface preheater (*viz.*, on the top, ninth, seventeenth

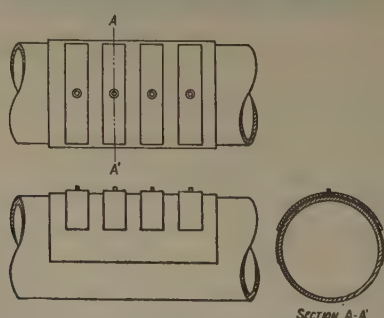


FIG. 6.—METHOD OF SUPPORTING TEST SPECIMENS ON SURFACE PREHEATERS AND ON SURFACE COOLERS.

and twenty-fifth tubes), in the segments of the holding tank, at four points on the surface cooler (*viz.*, on the top, ninth, seventeenth, and twenty-fifth tubes) and in the collection trough underneath the surface cooler.

In carrying out these tests, it was necessary that they should not interfere with the operation of the plant. Also, it was necessary to avoid the possibility of galvanic action, and to do so in such a manner as would insure that the test specimens were exposed as nearly as possible under actual working conditions. To accomplish this, two different methods were utilized.

The method used in exposing specimens on the surface preheater and on the surface cooler is indicated in Fig. 6. A thin bakelite tube (about 1/16 in. thick) was cut longitudinally into two parts, one of which comprised a little more than half the tube. Small bakelite pins (about 1/8 in. dia.) were then set into the larger portion of the tube as indicated in Fig. 6. Before the surface heaters or surface coolers started operating, the section of bakelite tubing was snapped in place on the top side of the proper tube. Then, curved specimens, which were about an inch wide and had a 3/16-in. dia. hole drilled in the center, were set in place over the bakelite pins in the tube. At the conclusion of the day's run, about 8 hr. later, the specimens were removed, rinsed in water, scrubbed with a bristle brush, rinsed in alcohol-ether mixture, dried, and reweighed to determine loss in weight. The bakelite tube was also cleaned and made ready for the next day's run.

Spool-type Specimen Holder

Quite a different method was used for supporting specimens in the holding tank and in the collection trough under the surface cooler. The supporting device, which is referred to as the "spool-type specimen holder," is shown in Fig. 7 (*A*, as assembled for 12 specimens; *B*, carrying case for separate parts). It is a very useful apparatus in the field-testing of metals. It was designed (1) to accommodate an easily prepared specimen of standard size; (2) for flexibility as to the number of specimens it will hold; (3) so that the parts are permanent in character or easily replaced; and (4) sufficiently compact that it can be carried or shipped as easily as ordinary hand luggage. The carrying case (Fig. 7*B*) will hold sufficient specimens and parts to assemble at least seven specimen holders (Fig. 7*A*).

The dimensions of the various parts used in assembling the spool-type specimen holder are given in Fig. 8. The disks (*A*) are of isolantite, or bakelite. The insulator (*C*) of the supporting rod is made of bakelite tubing. The supporting rod (*B*), the bracing rods (*E*) and the nuts are made from pure nickel. In assembling the apparatus, the insulator (*C*) is slipped over the supporting rod (*B*). Then, a disk (*A*) is slipped over the insulator. Standard insulating (isolantite or bakelite) spacers (*D*) and specimens are slipped alternately over the insulator (*C*) until all the specimens and spacers are in place. Another disk (*A*) is put on and a nut attached to the free end of the supporting rod (*B*). Then

four bracing rods (*E*) are slipped through the smaller holes in the disks (*A*) and nuts attached. Then, the assembled parts are screwed tightly together by means of nuts, after which the apparatus is ready for use.

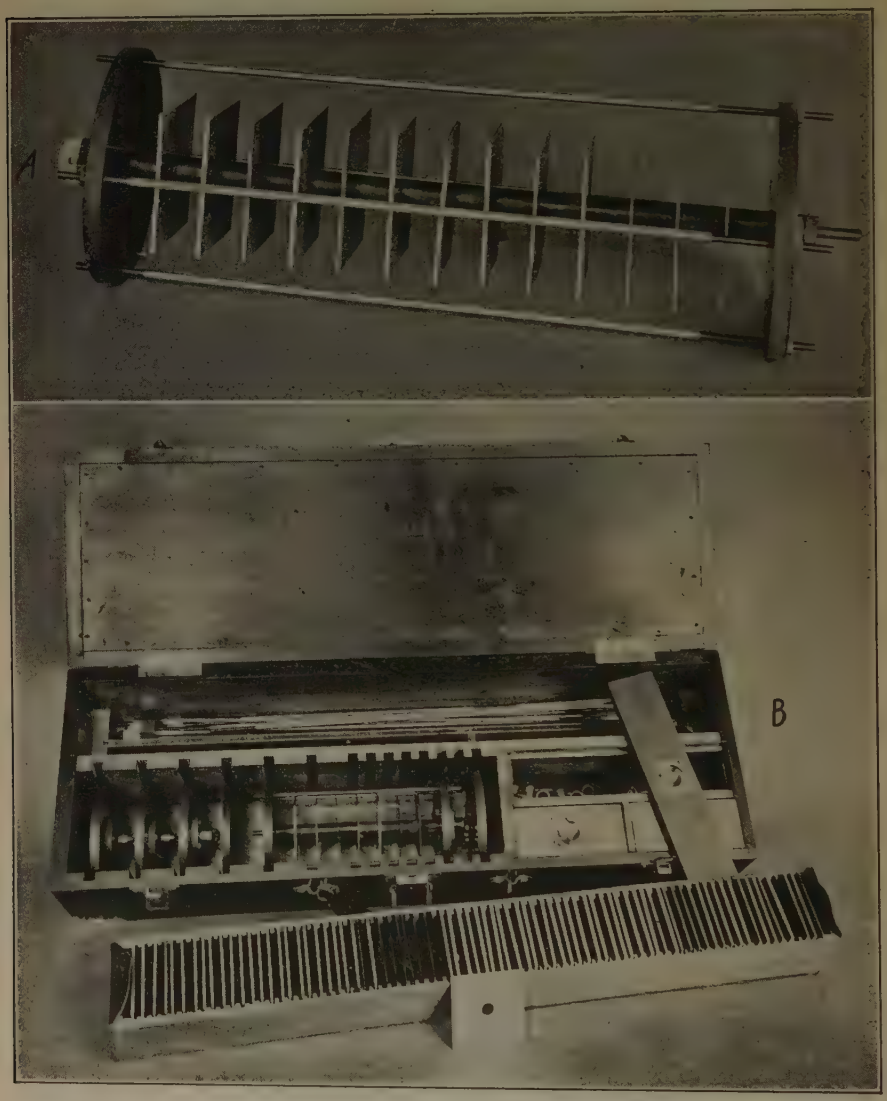


FIG. 7.—SPOOL-TYPE SPECIMEN HOLDER FOR SUPPORTING TEST SPECIMENS IN TANKS, ETC.; *A*, AS ASSEMBLED FOR 12 SPECIMENS; *B*, CASE FOR SEPARATE PARTS.

When the apparatus is assembled, the specimens are parallel and spaced ⅝ in. apart. All specimens are insulated from one another. The possibility of contact with exterior metallic objects is minimized by the

disks (A) and by the bracing rods (E). Also, the disks (A) and bracing rods (E) minimize the danger of accidental damage of the specimens by mechanical means.

Specimens were exposed to the action of milk for about 8 hr. in both the holding tank and in the collection trough under the surface cooler. In the holding tanks, the specimens were completely submerged, except for about 2 min. during each hour. In the collection trough, the specimens were always submerged.

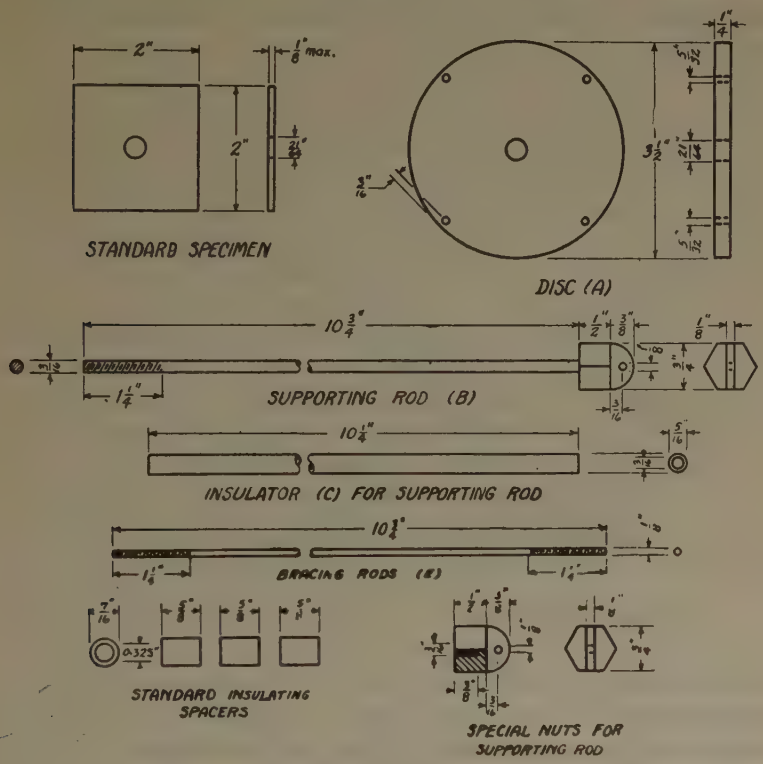


FIG. 8.—DIMENSIONS OF PARTS OF SPOOL-TYPE SPECIMEN HOLDER.

DATA OBTAINED AND DISCUSSION

The influence, on corrosion, of temperature, rate of flow, air and protective coatings was demonstrated in a striking manner by the series of tests which have been outlined.

On the surface preheater, no weighable losses were obtained. Examination of the specimens showed that the surfaces of the metal and the bakelite tube were covered with a thin film of casein, which evidently had been precipitated by the hot metal tube which was heated by the hot water flowing through it. The coating was white in color. It was

quite different from the brown-colored protein coating referred to in Part I. The casein coating was almost invisible but it served as an excellent protective coating for the underlying metal. An examination of the outer surface of the tubes comprising the preheater established that a similar deposit was present on them. This observation was of considerable importance in explaining why surface preheaters and surface coolers were not affected in the same manner by the action of the milk flowing over them.

On the surface cooler, no such casein deposit was developed, probably because heat was being withdrawn from the milk by the cold tube

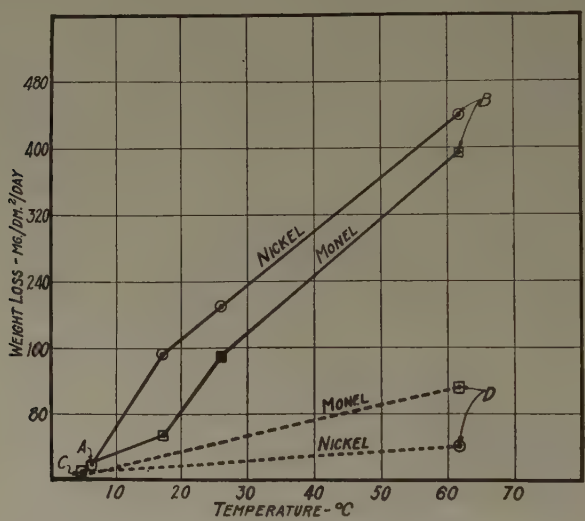


FIG. 9.—WEIGHT-LOSS DATA ON NICKEL AND MONEL METAL.

which was cooled by the liquid within it. In all cases, definite losses in weight were obtained, as well as a brownish discoloration. The data on nickel and monel metal are presented graphically in Fig. 9 by the lines marked *AB*.

It will be recalled that the hot milk flows from the multiple-segment holding tank to the surface cooler. The milk is at the same temperature in the holding tank as it is at the top tube of the surface cooler. The data obtained in the tests carried out in the multiple-segment holding tank are plotted also in Fig. 9; they are represented by the points marked *D*.

The data obtained in the tests carried out in the brine-jacketed collection trough underneath the cooler are plotted also in Fig. 9, and are represented by the points marked *C*.

It will be noted that the corrosion rate is higher at the higher temperatures. Most noticeable is the wide divergence between the line *AB*

and the line made by joining the two points *C* and *D*. The divergence is caused by the difference in the conditions of exposure, particularly the influence of air and the rate of flow of the milk. In the holding tank and in the collection tank the milk is in a state of very slight agitation, but on the surface cooler it is flowing rapidly. Also, the milk is applied to the top tube of the cooler in fine jets and flows over it in a very thin film which is freely exposed to air. The conditions are very favorable to the solution of air in the milk while it is being applied in small jets to the top tube and during its passage over the cooler. In the holding tank the milk is exposed to only a limited amount of air because the tank is provided with a heavy cover and there is a slight outward pressure in the vapor space above the milk.

As indicated in the preceding paragraph on coolers, the specimens were discolored with a brown-colored tarnish whenever there was a weighable loss. In making weight-loss determinations this discoloration was removed by scrubbing the specimen before reweighing. Therefore, the weight losses plotted in Fig. 9 represent the sum of the weight of metal contained in the tarnish and the weight of metal which was dissolved, or carried away, by the milk. To obtain information as to how much metal was absorbed by milk processed in nickel, samples of milk were collected at different points in a similar plant which was completely equipped with nickel apparatus. The bottled milk was found to contain 1.3 p.p.m. of nickel. Using data obtained in the weight-loss tests, it was estimated that about 21 per cent. of the total weight loss found its way into the milk, the balance was removed from the surface of the metal during the cleaning operation, in the form of discoloration. Also, it was found that the milk picked up 42 per cent. of its metal during its passage over the surface cooler.

The results obtained by field tests on surface preheaters, in holding tanks, and on surface coolers, demonstrated clearly the pronounced effect of such factors as protective coatings, rate of flow, air, and temperature, on the corrosion of metals by sweet milk during its pasteurization. It is a typical example of the importance of conditions in the corrosion of metals. The results suggest certain improvements in the method of handling milk and in the design of equipment.

Field Investigations in Milk Condensery

The influence of air on the corrosion of metals was demonstrated further during a field investigation carried out in a milk condensery, the product of which was evaporated milk.

Vacuum evaporators made of copper are employed in the production of evaporated milk. The general method of construction is indicated in Fig. 10. In their operation, preheated raw milk is drawn continuously into the evaporator, where it boils vigorously, at 140° F., under a 25-in.

vacuum. The evaporated milk is drawn continuously from the evaporator through a check valve and low-pressure pump. The evaporator is kept about half-filled with liquid. The quantity of raw milk handled is about 12,000 lb. per hr. The duration of the day's run depends on the amount of milk received at the plant. At the conclusion of the day's run, the inside of the evaporator is thoroughly cleaned.

Specimens were supported on the spool-type specimen holder already described and exposed at the points indicated by the crosses in Fig. 10. Three tests were made at each point, two specimens of each metal being included in each test. At the top of the evaporator, where the specimens were bathed in the vapors and spray from the condensing milk, the corrosion rates for nickel, monel metal, and copper were respectively 11, 15 and 48 mdd. At the middle point the rates were respectively 2, 4 and 33 mdd., and at the bottom point respectively 5, 5 and 24 mdd.

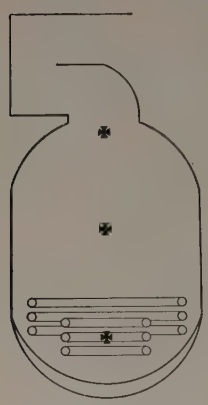


Fig. 10.—Vacuum evaporator for production of evaporated milk; outline of construction.

It is evident that the corrosion is greatest in the vapor space where there is liable to be the largest amount of air. A comparison of the above data with that given in Fig. 9 shows an impressive difference between the corrosion rate of nickel and monel metal in vacuum evaporators and on surface coolers. Except for the influence of air, the other conditions are similar.

Field Investigation in Plant Producing Cultured Milk Products

An indication of the importance of acidity on the corrosion of metals was obtained during a field investigation carried out in a dairy which produced cultured buttermilk from the skim milk discharged by the cream separators.

Buttermilk is made from skim milk by a ripening or fermentation process. A typical buttermilk machine is shown in Fig. 11. It consists of a tank which is heavily insulated on all sides to prevent loss of heat. It is equipped with a metal coil which can be rotated. The coil is so arranged that either hot water, cold water, or brine, may be circulated through it at will.

In making buttermilk, a quantity of skim milk is run into the machine and pasteurized, at 170° F., for 1 hr., by circulating hot water through the rotating coil. The skim milk is then cooled to 68° F. by introducing cold water into the rotating coil. A quantity of specially prepared "starter" containing suitable bacteria is then introduced into the batch and mixed thoroughly with it. The coil is then stopped and the batch is allowed to ripen for about 16 hr., at 68° to 70° F. During

the ripening period, the acidity of the batch increases about 0.7 per cent. and the batch assumes a jellylike consistency. At the proper time, the batch is cooled as quickly as possible to about 40° F., by introducing cold water or brine into the coil, which is rotated during the cooling process. A buttermilk of creamy consistency is discharged from the machine as soon as possible after it is cooled.

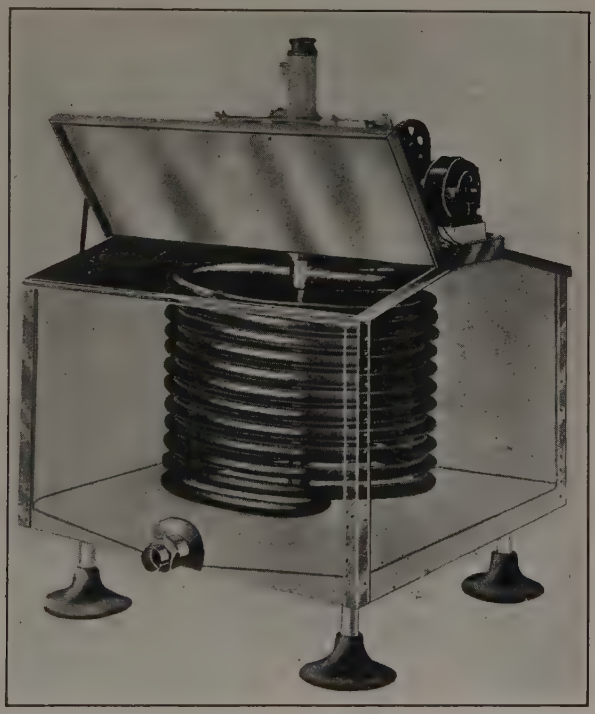


FIG. 11.—MACHINE FOR MAKING BUTTERMILK FROM SKIM MILK.

Specimens supported on the spool-type specimen holder were suspended in the batch at the start and removed just before discharging it from the machine. The rates of corrosion of nickel and monel metal were respectively 96 and 46 mdd. In both cases, the specimens acquired a brownish discoloration which was removed before the specimens were reweighed.

A comparison of the above data with that given in Fig. 9 indicates that the effect of much higher acidity was not great enough to offset the lack of air and continuous agitation, which played such an important part on the surface cooler handling sweet milk, of which the acidity is 0.1 to 0.2 per cent.

In order to obtain some information as to the amount of metal in finished buttermilk, samples were obtained for analyses from machines

constructed entirely of nickel. The buttermilk was found to contain 1.4 p.p.m. of nickel. Using the weight-loss data previously obtained, it was estimated that the metal removed from the machine during its cleaning, in the form of discoloration, represented 97 per cent. of the total loss in weight.

Field Investigations on Flavor of Milk

In Part I of this paper, reference has been made to the question of how metals influence the flavor of milk and milk products. At least in certain cases, the metal is held to be the cause when actually it is not associated with the production of foreign flavors. For example, in one of the cases investigated in the field, the dairyman was obtaining an unmistakable off-flavor in his pasteurized milk after it had been bottled and stored for about 20 hr. at about 40° F. A nickel pasteurizer was suspected of causing the off-flavor. This contention was proved erroneous when the dairyman's milk was taken to a neighboring dairy and pasteurized in glass-lined equipment. The flavor followed the milk. Also, milk from the neighboring dairy was pasteurized in the nickel machine and found to be normal in every respect, as had been usual. Further investigation showed that the feed of the cows was responsible for the off-flavor.

No case has ever been encountered in which nickel was associated in any way with off-flavors in milk. As has been pointed out by Quam and Soloman, Hunziker and Hosman, Rice, and Davies and Mattick,[13] copper and iron are associated sometimes with off-flavors in sweet milk and in other dairy products.

An interesting example of how copper may be associated with off-flavors in milk was obtained during a field investigation of an unusual case involving the use of monel metal milker pails. The pails were used on a farm which specialized in the distribution of raw Jersey milk of excellent quality. After successfully using the pails during the summer months, trouble was encountered in the early winter with a peculiar oily flavor which did not develop until after the raw milk had been stored in sterilized glass bottles at 40° F. for about 16 hr. Investigation proved that milking into sterilized monel metal pails caused off-flavors to develop which did not develop on milking into glass or tin. There was no appreciable metallic contamination of the milk during its short contact (about 20 min.) with the monel metal pail. Analyses showed that the metallic contamination was considerably less than 1 p.p.m. Further investigation showed that if the affected milk was pasteurized before storing, no off-flavor was apparent after the usual storage period. Bacteriological tests showed that the milk was not normal. Some strain of bacteria having an optimum growth point of about 40° F. was present

[13] See bibliography at end of Part I.

in the milk. Apparently, the bacteria were the primary cause of the off-flavor, but contact with copper, or the presence of minute amounts of copper in the milk, was necessary to their growth.

Part III.—General Discussion and Conclusions

By Robert J. McKay

From the considerations previously presented in this paper and others it is possible to list the qualities of importance in connection with the corrosion-testing of metals used in handling milk. In preparing this list the most important qualities are put first, but every quality is necessary and none can be omitted. The list follows:

1. Availability in all shapes and workability by all forming and seaming methods.
2. High mechanical properties.
3. Resistance to abrasion and impact.
4. Resistance to corrosion.
   (*a*) By milk.
   (*b*) By brines.
   (*c*) By natural waters.
   (*d*) By sterilizers and cleaners.
5. Lack of effect on milk.
   (*a*) Toxic.
   (*b*) Taste.
6. Resistance to delayed corrosion.
   (*a*) Corrosion-fatigue.
   (*b*) Corrosion-cracking.
7. Ease of cleaning.
8. Efficient heat transmission.
9. Appropriate color.

Allocation of Properties

The resistance to corrosion and related qualities bulk large in this list. As compared with other instances of corrosion-resistant construction the factors determined by corrosion tests have a greater relative importance than is usual. As stated in the introduction the properties other than those determined by corrosion test must be given full weight, but since the main purpose of this paper is the illustration of a method of corrosion-testing, those properties will be given only enough comment in this discussion to properly allocate them.

Availability and Workability

Due to the complicated nature and changing design of dairy apparatus the requirements under this heading are very broad. It should be noted

that all forms, working processes and seaming methods are included. Those that are not required at present may be necessary as designs are refined and improved. Nickel and monel metal fulfill these requirements well. The development of proper seaming methods has required much thought and testing including a large number of corrosion tests. These were principally on electrolytic effects and resulted in the selection of seams quite free from such effects.

High Mechanical Properties

A metal of proper structural strength is necessary for strong, light design. A minimum of space is desirable because a situation in the crowded sections of cities and towns is often convenient. These metals stand high in this respect. In a few cases particular properties are somewhat too high for the greatest facility in working.

Impact and Abrasion Resistance

The operations of cleaning subject milk-handling apparatus to an unusual amount of abrasion and impact. The material used must be able to withstand this without deformation or deterioration. Impact tests give exceptionally high results on nickel and monel metal. Abrasion tests, like corrosion tests, must be specific to the conditions, but from some years of observation of these metals in service it may be concluded that they are more resistant to these conditions than other materials which have been used.

Resistance to Corrosion

Corrosion by Milk.—Under this head we will consider the effect of corrosion on the metals in so far as it affects the life of equipment. Some of the tests used here are also used for the conclusions under 5 and 6, but the perspective is different, and the two separate viewpoints should be clearly understood. An illustration of the difference is the evaluation of corrosion rates in economic terms. In these tests, in which there is very little pitting or other local corrosion, the latter can be neglected and it is a simple arithmetical calculation to convert the unit used, mdd., to years of service of a given thickness of sheet, tube or rod. This is all that is necessary to determine the life of equipment, but to determine the effect of the metals on the milk from these data is a much more complicated matter which involves less exact and positive estimating methods.

Assuming that the average gage of sheet and tube used, as designed for proper strength, is 0.03 to 0.06 in. (22 to 16 gage) and 2 years is the absolute minimum allowable life of equipment, then the maximum allowable corrosion rate is 100 mdd. This gives a safety factor of from

1 to 2. For many types of equipment a corrosion life of from 10 to 15 years is desirable. In these cases the corrosion rate should be 20 mdd. or less.

Six controlling factors in corroding liquids, and therefore in corrosion-testing, are mentioned in the introduction of this paper, and their effects in the present case are summarized in Part I. Two of these have been understood for many years but four have only come into recognition since 1922. The practical value of considering these in corrosion studies seems to deserve emphasis and they are listed and briefly summarized below:

1. *Electrolytic Effects.*—Of little or no significance on nickel; some specific but relatively unimportant effect on monel metal.

2. *Oxygen Content.*—Increases corrosion seriously at some temperatures, reduces it at others.

3. *Acidity.*—Important though varying effects, usually accelerating but depending on other factors.

4. *Temperature.*—In most cases of the greatest importance, in a few unimportant; extraordinary accelerating effect when combined with other factors.

5. *Solid Films.*—Corrosion product films are of little effect; distinctive milk constituent films important in special cases.

6. *Movement.*—Great accelerating effect at high temperature and oxygen content.

In addition to these general factors there is a specific one of variation in the composition of the milk. The varying constituents were found to differ greatly in their effect on the corrosion reactions. It is obvious that an attempt to determine the effect of milk by study of any single constituent such as lactic acid will lead to improper conclusions.

The absence of electrolytic effects of any major importance in this type of corrosion is worthy of consideration. The principle phenomena can not be explained by electrolytic reasoning and apparently could not be studied by electrolytic tests. It is recognized that this statement is in disagreement with those writers who have assumed that all corrosion is electrolytic. The writers who have accepted the latter hypothesis have been primarily interested in the corrosion of iron and its alloys, and it seems probable that their opinions are based largely on the corrosion of iron. Certainly the major portion of the destructive corrosion of iron and iron alloys is electrolytic and it is almost an inherent feature of high-iron alloys to be subject to electrolytic corrosion, particularly that type which one of the present authors has called concentration cells. It seems a general rule that the most destructive types of corrosion are electrolytic. It is considered a valuable quality of nickel and monel metal that they are quite usually free from these effects and the local attack and pitting which accompanies them.

The above general conclusions on the six factors are based largely on the laboratory tests. These tests showed not only the direction of variation of the several factors, and their interdependence, but also gave a quantitative idea of their relative importance. This knowledge, however, leads to the conclusion that the laboratory tests in themselves are incomplete. They gave corrosion rates both higher and lower than the limits we have set for economic operating practice. The controlling factors are not quantitatively reproducible in the laboratory as they exist in practice, except at prohibitive expense, and therefore it was found necessary to make tests in operating plants. In these plants the important factors vary in different parts of the plant. But with the preliminary results of the laboratory tests it was possible to determine readily where and how these tests were to be made. This enabled the planning of the series of plant tests described in Part II.

To cover the variation of the six factors readily a standard testing apparatus has been developed. It would have been difficult to obtain proper agreement in many of the field tests without this apparatus. It was particularly useful in certain parts of the process. In others an individual special arrangement of samples was necessary.

With these considerations in mind field tests were made which quite clearly outlined the principle facts of this corrosion and enabled a reasonably accurate conclusion as to its course and effects. Although this final determination was made by field tests it would have been impossible without the foundation knowledge obtained in the laboratory studies.

The graphs and text of Part II show the quantitative results, which indicate that of the many parts of milk-handling apparatus there is only one wherein the corrosion rate extends beyond the estimated point of economy. This is on the tubes of the surface cooler. It is an interesting detail, illustrative of the ever-present danger of error from partly controlled or incomplete tests, that the rate varies on this surface cooler through a wide range, being 27 times as great at the top as at the bottom. Also the dividing line (100 mdd.) between impracticality and practicality of use lies well between the two, the rate at the top being 440 per cent. and that at the bottom only 18 per cent. of the danger point.

There has been interrelated use of data between the laboratory and field tests in many other ways. Another useful result obtained in the factory tests which might not have been obtained by laboratory tests alone, is that of the protective casein coating always formed on the surface preheater. This is a factor individual to milk and to this type of apparatus. It was not predicted by the laboratory tests and appeared only in the special tests in the plant but its identification depended on the laboratory data. The film was practically invisible and was found only by a process of elimination based on the knowledge obtained in the laboratory of the action of the other five factors.

Corrosion by Brines, Natural Waters, Sterilizers and Cleaners.—The use of these materials in the dairy is so general and so necessary that consideration of their corrosion effects is only second in importance to those of the milk itself. The data on rates have been determined in tests other than those reported here, and vary from 1 to 30 mdd., thus being well within the safety limits.

Effect on Milk

There is probably no common article of commerce so easily affected seriously by outside influence as milk. The slightest change often results in its complete rejection. For this reason it illustrates well the significance of the effect of corrosion products. As previously stated, these effects are more complicated and more difficult to measure than length of life, and for their consideration one must view the corrosion-test results in an entirely new light. To illustrate the interesting problems connected with this angle of corrosion some common instances are listed below. In milk, corrosion products may affect the wholesomeness, the taste, or the color. Other cases are changes in coloring materials, contamination of other human foods, changing appearance of objects of art or architecture, lowering the purity of c.p. chemicals such as caustic soda for artificial silk. Such effects have broad significance.

Toxicity.—Toxicity is a matter of such variation that its accurate measurement is difficult. A large number of experiments on this subject are quoted in Part I. It is believed that they furnish a safe basis for conclusions. We can say that nickel contents up to 100 p.p.m. cannot do harm to the human system. Probably much larger concentrations are entirely harmless. The legal limit for the copper content of foods is 30 p.p.m. Accepting these figures as reliable the simplest and most positive way of determining this effect was actual analysis of nickel and copper contents in operating factories. The highest amount of nickel found under any conditions was 15.7 p.p.m. and the average content in bottled milk handled entirely in nickel was 1.3 p.p.m. These figures are in agreement with those estimated from laboratory and field corrosion tests. The amounts of copper found were in all cases less than those of nickel. They are so far below the safety limit that toxicity is obviously a factor which can be disregarded. It is much less important for study than the life of equipment, since a rate of corrosion sufficient to wear out the apparatus rapidly will not be sufficient to produce concentrations even approaching the allowable limits.

Taste.—The flavor of milk is one of the best methods of determining its wholesomeness. No unpleasant or even unusual flavors are allowable. Pure nickel in the amounts given above cannot affect the flavor. Neither will the copper from monel metal affect the flavor directly. However, under special conditions monel metal may have an effect. This may be

due to electrolytic effects producing deterioration of tinned copper equipment to which it is electrically connected, and also the small amount of copper dissolved may catalyze bacterial growths which produce off-flavors. These occurrences are unusual, as the use of tinned copper equipment with monel metal is rare and the presence of the bacteria which produce off-flavors should be avoided for other reasons.

Resistance to Delayed Corrosion

The length and conditions of service required in milk handling make it necessary to be certain of freedom from corrosion-cracking and fatigue. Other tests and experience with monel metal and nickel early led to the conclusion that laboratory tests on these factors would be unnecessary because of the high values of the corrosion-fatigue limit and the absence of corrosion-cracking. Field examination of equipment in service for periods of from 5 to 18 years has strengthened this conclusion.

Ease of Cleaning

Cleanliness in dairy work is exceptionally necessary since any residues of milk products or other materials carried from one batch to another are sources of infections, off-flavors and unwholesomeness. A high standard of cleanliness is relatively easy to maintain on nickel and monel metal because of their smooth finish in service, but if once allowed to become dirty or tarnished their resistance to corrosion and abrasion make cleaning difficult. Because of this it was necessary to develop a suitable cleaner for the individual needs of these metals and this has been done, using the results of the tests reported here and others. With this mixture cleaning is easy and complete.

Efficient Heat Transmission

As previously described rapid heating and cooling of milk is one of the most important processes. The heat conductivity of nickel and monel metal is not high but due to the possibility of maintaining clean, scale-free surfaces the overall heat transmission of heating and cooling coils and surfaces is highly efficient.

Appropriate Color

The color of the metal should be such that impurities and dirt are easily detected by inspection. Nickel and monel metal fulfill this requirement well when polished. Under use in certain conditions a tarnish develops which is undesirable in color. This tarnish is easily removed by the cleaner mentioned above.

General Conclusions

1. To be of practical value corrosion tests should be evaluated in conjunction with tests of other properties.

2. A proper combination of laboratory and service testing is usually necessary before selection of the best metal and design for corrosion-resisting construction.

3. Six extra-metal factors should be controlled or corrected for in corrosion tests: (1) Electrolytic effects; (2) oxidizing agents, usually dissolved air; (3) acidity; (4) temperature; (5) solid films; (6) movement.

4. A standard apparatus, such as described, is suitable for many field tests. Its use must be guided by considerations of the six variable factors and where necessary it must be replaced by specially designed tests.

5. Useful conclusions can be reached by the above plan. Conclusions reached by shorter methods are liable to be misleading.

6. Corrosion tests indicate that both nickel and monel metal are suitable for handling milk. Nickel is usually preferred to monel metal. This is in spite of the fact that its corrosion rates are higher (see conclusion 1 above).

7. Both metals pass the requirements of working qualities, mechanical strength, resistance to corrosion-cracking and fatigue, abrasion and impact, ease of cleaning, heat transmission and appropriate color.

8. Due to the type of corrosion of milk on nickel and monel metal the electrolytic features of corrosion can be neglected. This is a special case. Where pitting and local corrosion are the rule, as in iron alloys, these features must not be neglected.

DISCUSSION

C. G. Fink, New York, N. Y.—Was the milk analyzed for copper before testing?

O. B. J. Fraser.—Results are given for nickel only. I was not interested at the time in copper. I made no analytical determinations of metal in the milk. They have been made in other laboratories.

C. G. Fink.—But you did record that the amount of copper was somewhat less than that of nickel.

O. B. J. Fraser.—That was not my own result.

C. G. Fink.—The copper might be less after the test than before. In the presence of nickel, copper deposits out by cementation.

O. B. J. Fraser.—I do not know whether copper would be less after tests or not, but I believe not. Its behavior in milk would be quite different from that in pure lactic acid solutions, for in milk the metals are locked up in combination with proteins, and I do not believe that copper could be removed from such combination by cementation on another metal.

C. G. Fink.—Add a little more lactic acid and it will help.

Correlation of Laboratory Corrosion Tests with Service: Weather-exposure Tests of Sheet Duralumin*

By Henry S. Rawdon,† Washington, D. C.

(New York Meeting, February, 1929)

Any laboratory corrosion test, as judged from the practical point of view, is valuable only to the extent that it foretells what will, in all probability, occur in service. Such a test is most properly to be considered as a "pilot test," that is, a test which indicates the direction along which action may be expected to occur rather than as a truly quantitative test which would be expected to tell just how and to what extent the action would proceed. It is generally recognized that laboratory corrosion tests should be chosen with particular reference to the character of service expected for any particular type of metal, so far as it can be foreseen. Even when this requirement has been fulfilled, however, the question whether the actual service behavior of the material is in accordance and general agreement with predictions based upon such laboratory tests is always a pertinent one. The information available in the technical literature bearing on the correlation between the service behavior of metals from the corrosion standpoint, and the results obtained with the same metals in laboratory corrosion tests is very meager, indeed.

The results which have been obtained in weather-exposure tests of sheet duralumin which form the body of this discussion are presented here for their bearing on this particular phase of the problem of the corrosion resistance of duralumin. Although the exposure tests described have not been completed, in the sense that all of the tests, in the series initially laid down, have been accomplished, still the general trend shown by the results is so clear that a number of definite conclusions at this stage (subject, of course, to possible modification in the light of later results) are believed to be warranted. The tests reported upon here form one phase of the much broader study of this subject which has been under way for several years in which the National Advisory Committee for Aeronautics, the Bureau of Aeronautics of the Navy Department, the Army Air Corps and the Bureau of Standards have cooperated. Without the very helpful cooperation of the manufacturers in furnishing the

* Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce

† Metallurgist, Bureau of Standards.

materials, which in some cases were made especially for this work, the investigation would have been very seriously handicapped.

The fact is now well established that some sheet duralumin,[1] as well as some other high-strength aluminum alloys, under some conditions of use do not maintain their initial properties without impairment. The change

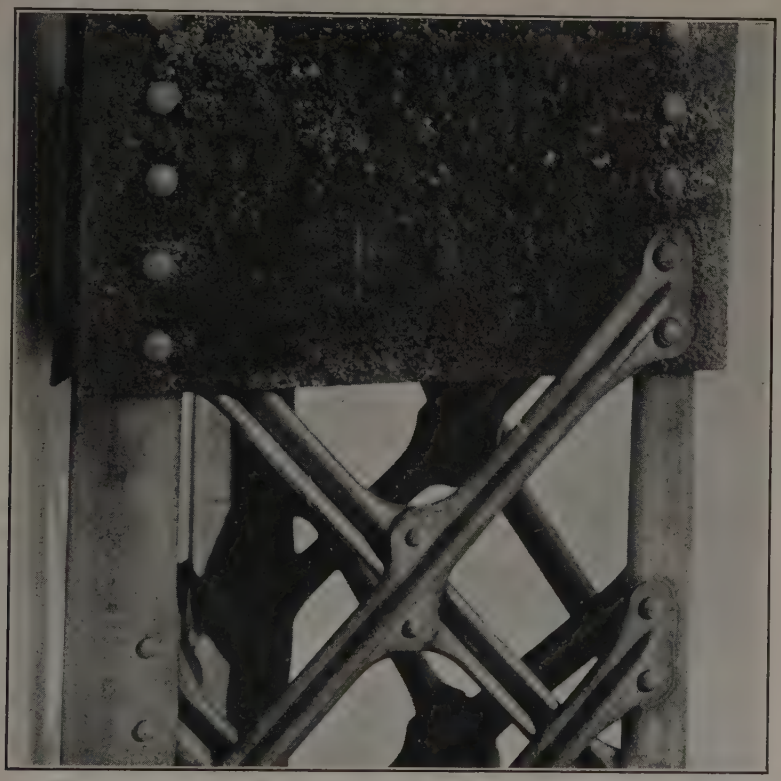


FIG. 1.—PART OF A DURALUMIN GIRDER OF TYPE USED FOR AIRSHIP CONSTRUCTION AFTER 3 YEARS' EXPOSURE TO ATMOSPHERE.

Steel end plates, which were added for test purposes, are severely rusted, whereas duralumin lattices and channels show no marked surface attack. Such duralumin, however, has occasionally been found to be very brittle.

may in some cases be very pronounced indeed. This change, as shown by the tensile properties, consists essentially in a marked lowering of the ductility of the material accompanied by a somewhat smaller proportional decrease in the tensile strength. Unlike the atmospheric corrosion of iron or steel, the change which may occur in sheet duralumin is not

[1] The name "duralumin" is used here as referring to the class of heat-treatable aluminum alloys in which the essential alloying elements are copper, magnesium, silicon and manganese and not to the product of any particular manufacturer.

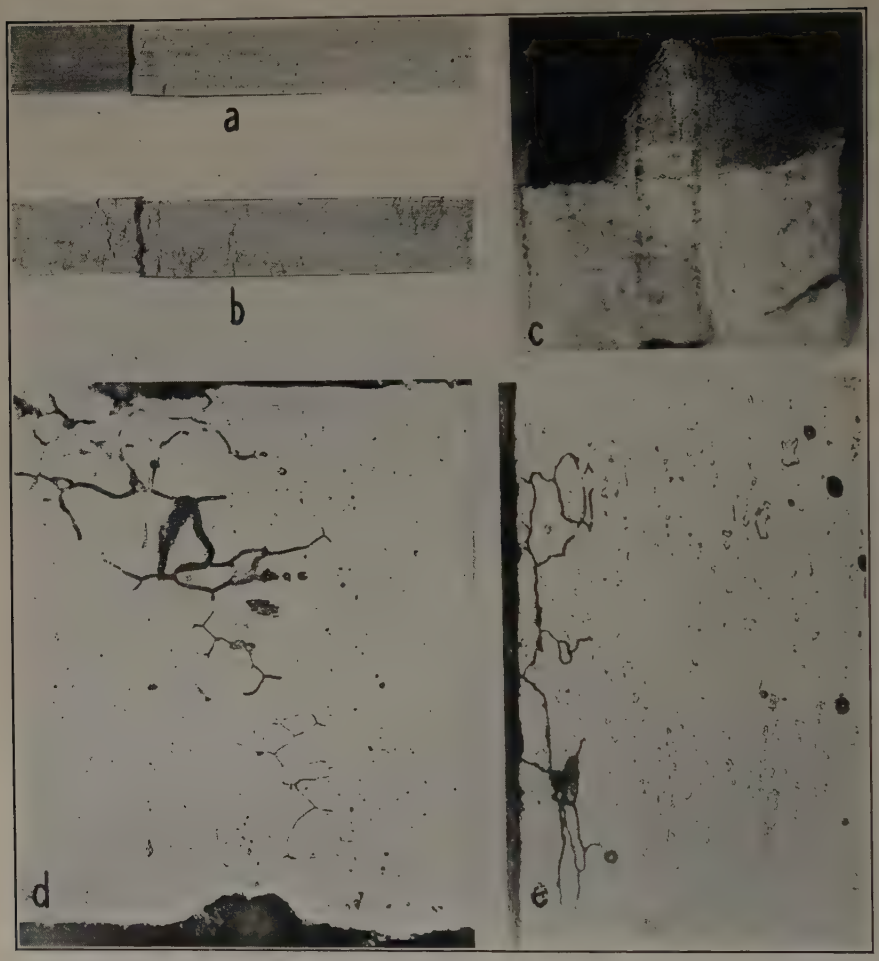


FIG. 2.—EFFECT OF INTERCRYSTALLINE CORROSION ON MECHANICAL PROPERTIES OF SHEET DURALUMIN.

a, Sheet (0.048 in.) after 1 year's storage indoors. × 2. Ultimate tensile strength, 55,000 lb. per sq. in.; elongation in 2 in., 16 per cent.

b, Varnished sheet (0.057 in.) exposed to weather 8 months. × 2. Ultimate tensile strength, 48,600 lb. per sq. in.; elongation in 2 in., 6.5 per cent.

Specified values for material of *a* and *b*, 55,000 lb. per sq. in., ultimate tensile strength; 30,000 lb. per sq. in., yield point; 18 per cent. elongation.

c, Sheet material (0.012 in.) used as an airplane wing covering exposed 2 years to sea air, severely bent to show degree of embrittlement. × 2½.

d, Cross-section of material of *c*, unetched. × 250.

e, Cross-section of a sheet of duralumin after several years' storage indoors, showing slight intercrystalline attack. × 500.

(Figure reduced to ⅘ original size.)

accompanied by any very marked surface indications. Sheet duralumin which has become brittle in service may not show any more evidence of the change in its surface appearance than is shown by the specimen in Fig. 1. In some exceptional cases, sheet material has become so weak and brittle that it could be broken readily with the fingers.

The very extensive and successful use of the light aluminum alloys for aircraft has served in large measure to refute imputations which have been made at times concerning the unreliability and lack of permanence of this class of material. Experience has shown that most sheet duralumin under most conditions retains for years its initial strength and ductility unimpaired. With the increasing demands imposed upon the materials of modern aircraft construction, however, the question of the permanence of such materials becomes one of increasing importance and it was this aspect of the problem which prompted the study which was undertaken.

In Fig. 2 is shown the nature of the structural change whereby the impairment of sheet duralumin is brought about. It has generally been assumed that this change is a form of corrosive attack. The results of the many laboratory corrosion tests which have been made and also the weather-exposure tests discussed below support this assumption. There can be very little doubt, indeed, but that this is the true explanation of the phenomenon. The corrosive attack is not of the ordinary familiar type, however. The characteristic feature of this attack is that it is not merely a surface attack but a penetration into the "body" of the metal. The path followed is an intercrystalline one, the corrosion being localized almost entirely along the grain boundaries. For this reason, it is ordinarily referred to as "intercrystalline corrosion."

Résumé of the Results of Laboratory Tests

It is not necessary to report here in detail the results of the laboratory accelerated corrosion tests which largely constituted the early part of the investigation. These tests were carried out on full-size tension bars which after being corroded by repeated immersion (wet and dry test) in various corrosive solutions were tested in tension, the change in the tensile properties being used as a measure of the corrosive attack. This part of the study has already been reported upon[2] in detail elsewhere.

A short résumé of the important facts established by the laboratory study will suffice as a basis for the correlation of these results with those obtained in the weather-exposure tests. The results of the laboratory

[2] H. S. Rawdon: Corrosion Embrittlement of Duralumin. II, Accelerated Corrosion Tests and the Behavior of High-strength Aluminum Alloys of Different Compositions. III, Effect of the Previous Treatment of Sheet Material on the Susceptibility to this Type of Corrosion. IV, The Use of Protective Coatings. Natl. Advisory Com. for Aeronautics *Technical Notes.* Nos. 283, 284, 285.

corrosion tests of sheet duralumin have established, beyond reasonable doubt, the following facts:

1. The change in sheet duralumin whereby the material is rendered relatively weak and brittle is a corrosion phenomenon localized along the grain boundaries and not a "spontaneous" internal change within the alloy such as, for example, a delayed phase change.

2. While this effect has been produced in the laboratory to some extent at least, in all the compositions used, the presence of the constituent formed by the alloying of aluminum with copper appears to be most closely associated with this form of attack.

3. Chloride solutions are most potent in causing an intercrystalline attack. Solutions of the other halogens act similarly but are less active.

4. The rate of attack is accelerated by an increase of the temperature. At 70° C., the effect in dilute solutions was approximately four times that at room temperature in the same solutions.

5. The ordinary loss of weight method for determining the corrosion rate is not applicable in this problem. The testing of full-size tension bars after different degrees of attack is, by far, the best method to use. Certainly this method is practically the only one which will give reliable information as to the change in the mechanical properties of the metal, which is the information needed in this particular case.

6. In order to develop its highest tensile properties, duralumin must be heat-treated. The method by which the heat treatment is carried out is very intimately related to the susceptibility of the heat-treated duralumin sheet to embrittlement by intercrystalline attack. The heat treatment of duralumin consists of two operations, quenching and aging. Heat-treated sheet duralumin for which the quenching has been done in cold water is far more resistant to intercrystalline attack than the same which has been quenched in hot water before aging. Heat-treated material for which the aging process has been accelerated by using an elevated temperature is much less resistant than if the aging is done at room temperature.

7. Cold-working of sheet duralumin, by stretching, bending, and the like, results in a condition which is somewhat favorable to intercrystalline corrosion, but this feature is a minor factor as compared with the differences in corrosion resistance which may result from improper heat treatment.

8. Properly heat-treated sheet duralumin is not necessarily corrosion proof. Corrosion of the ordinary type may be expected to occur; hence the need of protective coatings.

9. Oxide coatings formed by electrolytic treatment ("anodic process") as well as similar related coatings afford only very little protection in themselves. They must be kept well greased. The type of grease

used is of secondary importance, the frequency of renewal is of prime importance.

10. Coatings of the spar varnish type are of only slight value. The addition of aluminum powder, however, reduces very greatly the permeability of such coatings by atmospheric moisture and also retards the deleterious effect of light on such coatings. Clear and pigmented varnish coatings as well as bitumastic enamel exposed in various solutions in laboratory corrosion tests failed by blistering. Aluminum-pigmented rubber coatings have given excellent performance in laboratory corrosion tests.

11. Metallic aluminum coatings produced either by the metal-spraying process or by rolling a duplex slab having a duralumin core and aluminum surfaces into sheet form, thereby producing a coating which forms an integral part of the finished sheet, have given most excellent results. Protection of the "cut" edges of aluminum-coated duralumin sheets appears not to be necessary if the sheet has been properly heat-treated.

Method of the Exposure Tests

The exposure tests, like those in the laboratory, were carried out upon full-size tension bars of sheet duralumin, 14-gage material being

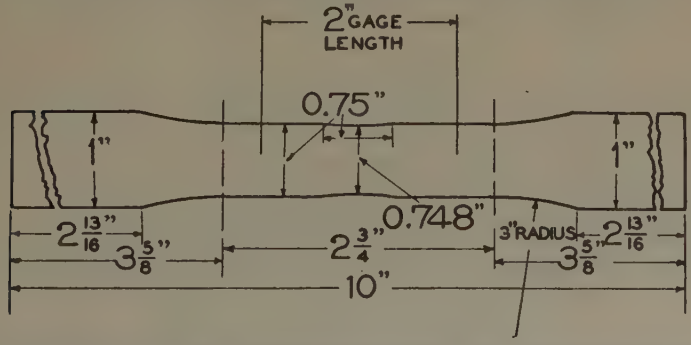


Fig. 3.—Dimensions of tension specimen of sheet duralumin (14-gage) used for accelerated corrosion tests and for exposure to weather.

used for nearly all of the tests. The dimensions of the tension specimens are given in Fig. 3. The chemical compositions of the different materials are summarized in Table 1.

The specimens to which coatings were applied before exposure were heat-treated by hot-water quenching. According to the laboratory tests, such material would be expected to show a relatively low resistance to corrosion, hence, a breakdown of the "protective" coating under atmospheric influences would be expected to be shown by the change in the properties of the basic metal at a relatively early stage.

TABLE 1.—*Sheet Alloys Used in Corrosion and Exposure Tests*

Designation of Material	General Nature of Material	Percentage Composition*										
		Cu	Fe	Si	Mn	Mg	Cr	Ni	Pb	Ca	Sn	Zn
17ST	Commercial alloy of the duralumin type (A. S. S. T. Handbook)	4.1	0.34	0.32	0.51	0.61	N.D.†	N.D.	N.D.	N.D.	N.D.	N.D.
BT	Commercial duralumin (A. S. S. T. Handbook)	3.9	0.51	0.31	0.58	0.60	<0.02	N.D.	N.D.	N.D.	N.D.	N.D.
25S	Commercial alloy sheet (described in A. S. S. T. Handbook‡)	4.2	0.45	0.9	0.68	N.D.		N.D.		N.D.	N.D.	N.D.
51S	Commercial alloy sheet (described in A. S. S. T. Handbook‡)	0.05	0.38	1.0	0.01	0.61		N.D.		N.D.	N.D.	N.D.
A-17ST	Commercial alloy sheet (described in A. S. S. T. Handbook‡)	2.5	0.28	0.24	0.02	0.40		N.D.				
B-17ST	Commercial alloy sheet (described in A. S. S. T. Handbook‡)	3.7	0.36	0.22	0.02	0.45		N.D.				
63A	Prepared by manufacturer for this investigation, Fe content higher than in ordinary duralumin	3.8	1.15	0.24	0.50	0.63		<0.02				
58B	Prepared by manufacturer for this investigation, intended as a "low-copper" alloy	3.1	0.55	0.21	0.50	0.63		N.D.				
I-1	Prepared by manufacturer for this investigation, low Fe-Si ratio	4.2	0.20	0.20	0.47	0.47		N.D.	N.D.	N.D.	N.D.	N.D.
I-2	Prepared by manufacturer for this investigation. Made from material of high purity, low Fe and Si contents	4.2	0.08	0.10	0.47	0.52		N.D.	N.D.	N.D.	N.D.	N.D.
I-3	Duralumin type of alloy (17S)	4.2	0.47	0.34	0.47	0.50		N.D.	N.D.	N.D.	N.D.	N.D.

* Chemical analyses by J. A. Scherrer, Chemist, Bureau of Standards.
† N.D. = not detected.
‡ 1929 edition, page 500.

The exposure test racks were installed at three different locations representative of quite widely varying weather conditions. The locations are as follows: Naval Air Station, Coco Solo, Canal Zone; Naval Air

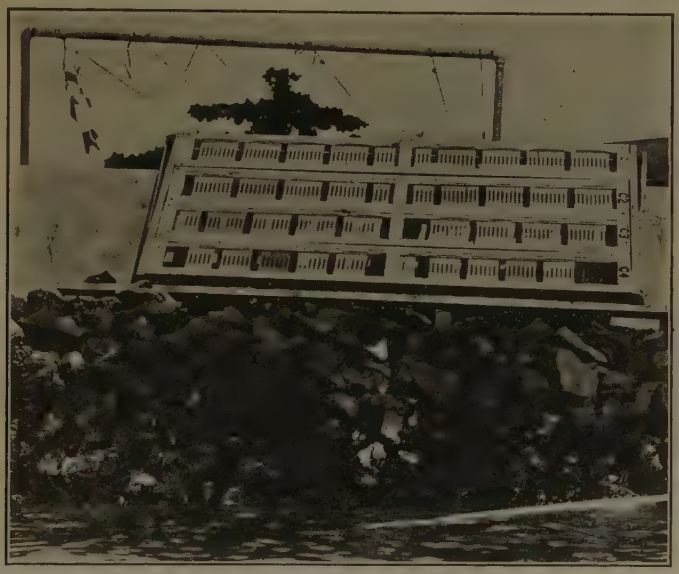


FIG. 4.—EXPOSURE RACK AND SPECIMENS, COCO SOLO NAVAL AIR STATION, CANAL ZONE.

FIG. 5.—EXPOSURE RACK AND SPECIMENS, BUREAU OF STANDARDS ROOF.

Station, Hampton Roads, Va.; and Bureau of Standards. The Coco Solo rack is illustrated in Fig. 4. This rack, inclined as shown, faced the south and was situated on the breakwater. The Hampton Roads rack was situated in a very similar manner on a platform attached to the

TABLE 2.—*Weather-exposure Test Specimens*

Set No.	Material*	Treatment Prior to Exposure: Quenching Temperature, Deg. C.	Time in Bath, Min.	Quenching Media	Aging and Coating	Initial: U. T. S., Lb. per Sq. In.	Elongation in 2 In., Per Cent.
1	17ST	500	15	Water 0° C.	Aged at room temperature	62,300	20.0
2	17ST	500	15	Water 25° C.	Aged at room temperature	63,600	22.0
3	17ST	500	15	Water 100° C.	Aged at room temperature	63,200	22.0
4	17ST	500	60	Water 25° C.	Aged at room temperature	63,100	20.0
5	17ST	500	15	Water 0° C.	Aged 24 hr. at 100° C	61,900	23.0
6	17ST	500	15	Water 0° C.	Aged 3 hr. at 150° C	58,700	21.0
7	17ST	500	15	Oil 0° C.	Aged at room temperature	60,800	20.0
8	17ST	500	15	Oil 25° C.	Aged at room temperature	62,500	20.0
9	17ST	425	15	Water 25° C.	Aged at room temperature	43,500	20.0
10	17ST	425	60	Water 25° C.	Aged at room temperature	48,400	19.0
11	17ST	425	5†	Water 25° C.	Aged at room temperature	46,700	20.0
12	17ST	500	15	Water 0° C.	Aged 1 hr. at room temperature and stretched 10 per cent. in length	56,800	11.0
13	17ST	500	15	Water 0° C.	Aged 96 hr. at room temperature and stretched 10 per cent. in length	65,800	12.0
14	17ST	500	15	Water 0° C.	Aged 3 weeks at room temperature and cold rolled 10 per cent. in length	70,400	11.0
16	17ST	500	15	Water 100° C.	Aged 96 hr. at room temperature and stretched 10 per cent. in length	65,600	11.0
17	17ST	500	15	Water 0° C.	Aged 96 hr. at room temperature and heated 5 hr. at 135° C	58,100	20.0
18	BT	500	15	Water 25° C.	Aged at room temperature	63,700	20.0
19	BT	500	15	Oil 25° C.	Aged at room temperature	64,500	20.0
20	17ST-A	500	15	Water 0° C.	Aged at room temperature	37,100	24.0
21	17ST-B	500	15	Water 0° C.	Aged at room temperature	51,500	22.5
22	I-1	500	15	Water 0° C.	Aged at room temperature	59,000	20.5
23	I-2	500	15	Water 0° C.	Aged at room temperature	57,400	20.0
24	63A	500	15	Water 0° C.	Aged at room temperature	51,800	19.5
25	58B	500	15	Water 0° C.	Aged at room temperature	51,700	20.0
26	25SW	520	15	Water 0° C.	Aged at room temperature	53,600	20.5
27	51SW	520	15	Water 0° C.	Aged at room temperature	53,700	27.5
28	17ST	500	15	Water 100° C.	Coating, varnish containing some chromate + aluminum paint	60,800	21.0
29	17ST	500	15	Water 100° C.	Coating, linseed oil pigmented with lampblack	60,700	21.0
30	BT	500	15	Water 100° C.	Coating, "Jirotka"	61,300	20.0
31	BT	500	15	Water 100° C.	Coating, "Jirotka" + lanolin	61,300	20.0
32	BT	500	15	Water 100° C.	Coating, anodic	62,400	20.0
33	BT	500	15	Water 100° C.	Coating, anodic + lanolin	62,600	20.0
34	I-1	500	15	Water 100° C.	Coating, grease + aluminum powder	59,700	20.0
35	I-2	500	15	Water 100° C.	Coating, aluminum-pigmented varnish	60,000	21.5
36	25ST	520	15 to 30	Water 100° C.	Aged 8 to 15 hr. at 140° C.; coating, varnish containing some chromate	59,500	25.0
37	25ST	520	15 to 30	Water 100° C.	Aged 8 to 15 hr. at 140° C.; coating, anodic + aluminum varnish	59,400	21.0
38	I-3	500	15	Water 100° C.	Aged at room temperature; coating, grease + aluminum powder	62,300	21.5
39	Alclad 17ST	None	As received			54,700	19.0

* The materials were made by the two American manufacturers of duralumin, that designated as BT by one manufacturer, all of the remainder by the other.

† Hours.

side of the pier, well above the high water line. The Bureau of Standards rack was located on the roof of one of the buildings and faced the south but, as shown in Fig. 5, was raised only slightly above the horizontal position. The test bars were held in place in the cypress exposure rack by a narrow strip of wood at each end of the bars together with an outer reinforcing strip of sheet aluminum, both of which were fastened to the rack by screws at intervals of a foot or so. In addition to these three sets of specimens, a fourth set was kept in the laboratory in sealed glass containers. Soda lime was used to maintain a dry atmosphere within the containers, the specimens being supported on end on a grid of galvanized wire mesh placed well above the soda lime.

No change was made in the position of the specimens in any way during the exposure period. Necessarily, the exposure of the two surfaces of the specimens was therefore not the same. In this respect, however, the exposure tests paralleled service conditions more closely than did the laboratory corrosion tests.

In Table 2 are listed the different specimens used in the exposure tests together with their initial tensile properties, and the treatment given to each, such as modifications in heat treatment, cold working, coating process and the like. Each set of specimens, representative of each of the different variables, consisted, in most cases, of 10 specimens. In a few cases, a smaller number was used.

Results

At successive intervals of several months, as shown in Fig. 7, one specimen from each set was removed for testing. The tensile properties of the exposed specimens were determined and an examination of the microstructure made to determine whether or not intercrystalline corrosion had occurred. The appearance of the specimens shown in Fig. 6 is typical of the results produced by exposure to the weather. In the Hampton Roads tests the surface change was somewhat less marked than was the case in the Coco Solo tests, and in the Bureau of Standards exposure specimens the change was very much less marked. It is quite evident from Fig. 6, without further discussion, that only in a qualitative sense can the surface appearance of the exposed bars be used as a measure of the effect of corrosion on the underlying metal.

The results of the tension tests of the exposed specimens, to date, are summarized graphically in Fig. 7. The initial properties, that is, those of the uncorroded materials, have been included throughout for all of the sets of specimens as a "base line" for comparison. In those cases in which the evidence of the occurrence of intercrystalline attack was indisputable, this feature has also been indicated.

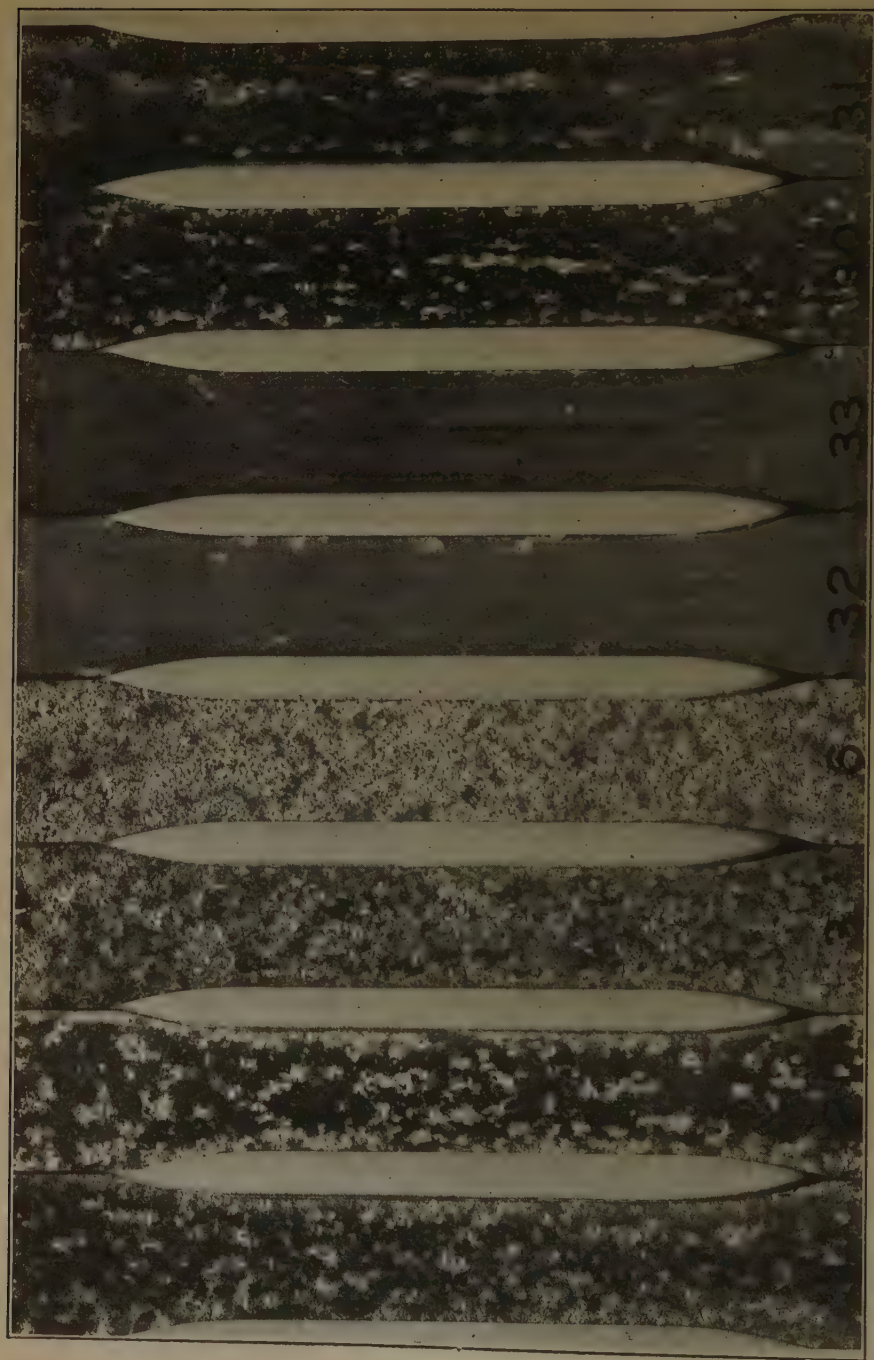


FIG. 6.—SURFACE APPEARANCE OF REPRESENTATIVE SPECIMENS FROM COCO SOLO RACK AFTER 4½ MONTHS' EXPOSURE.
Photograph shows under or partly protected surface of specimens. For significance of numbers, refer to Table 2.

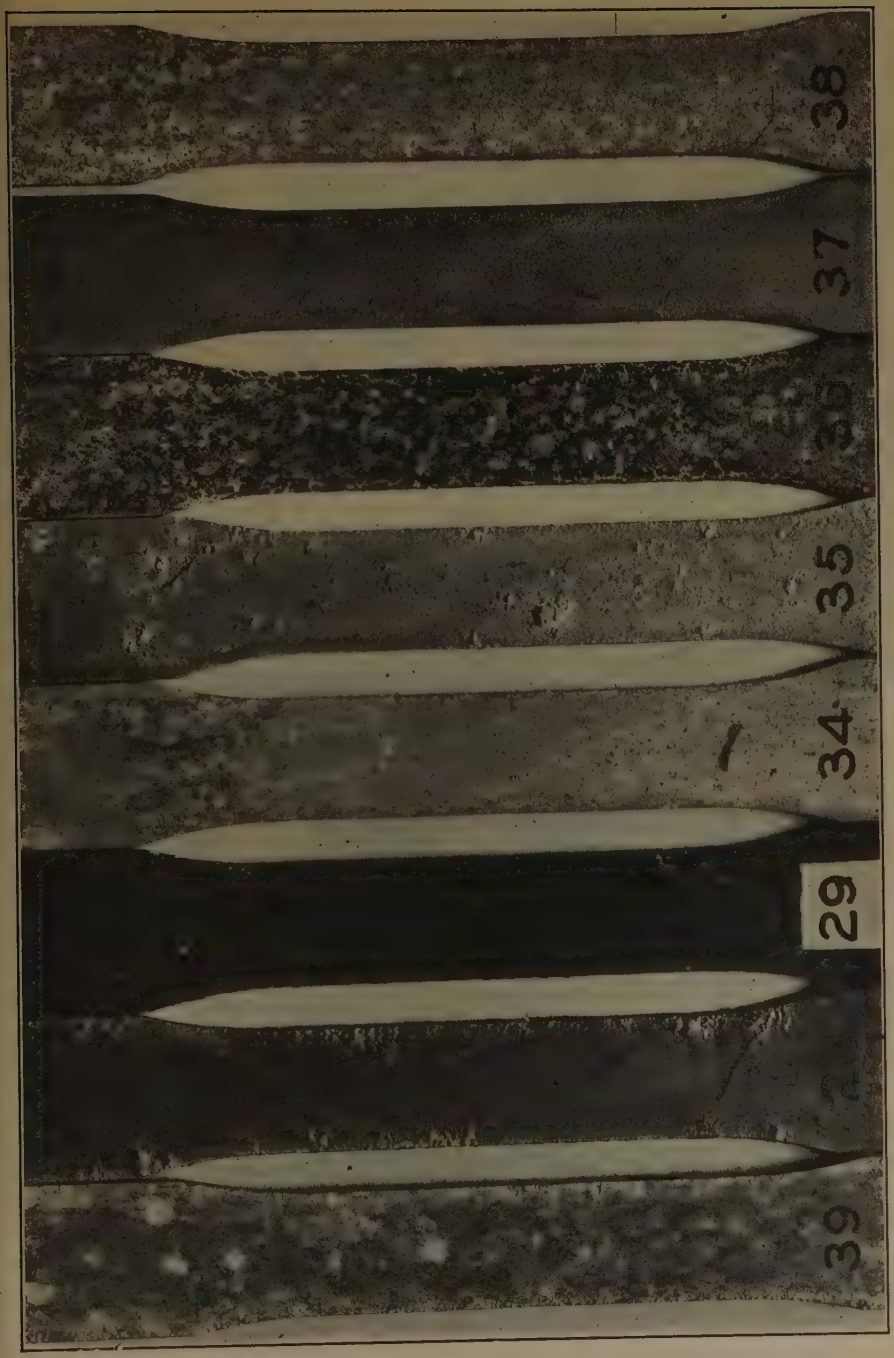
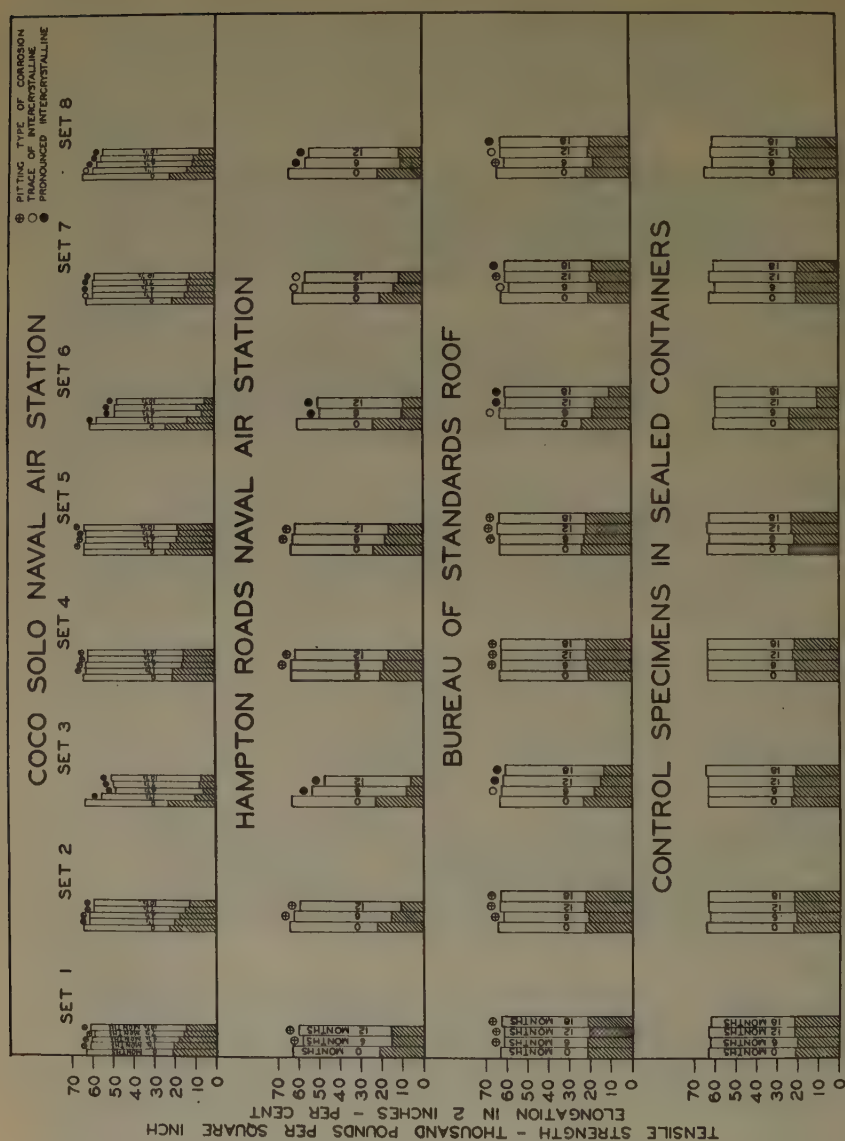


FIG. 6. (CONTINUED).—SURFACE APPEARANCE OF REPRESENTATIVE SPECIMENS FROM COCO SOLO RACK AFTER 4½ MONTHS' EXPOSURE.



WEATHER EXPOSURE TESTS OF SHEET DURALUMIN

FIG. 7.—SUMMARY OF RESULTS OF TESTS OF SPECIMENS OF SAME MATERIALS EXPOSED TO WEATHER IN THREE LOCATIONS AND OF "CONTROL" SPECIMENS. REFER TO TABLE 2 FOR TREATMENT OF MATERIAL PRIOR TO EXPOSURE. Height of large rectangle represents tensile strength, height of crosshatched portion, elongation.

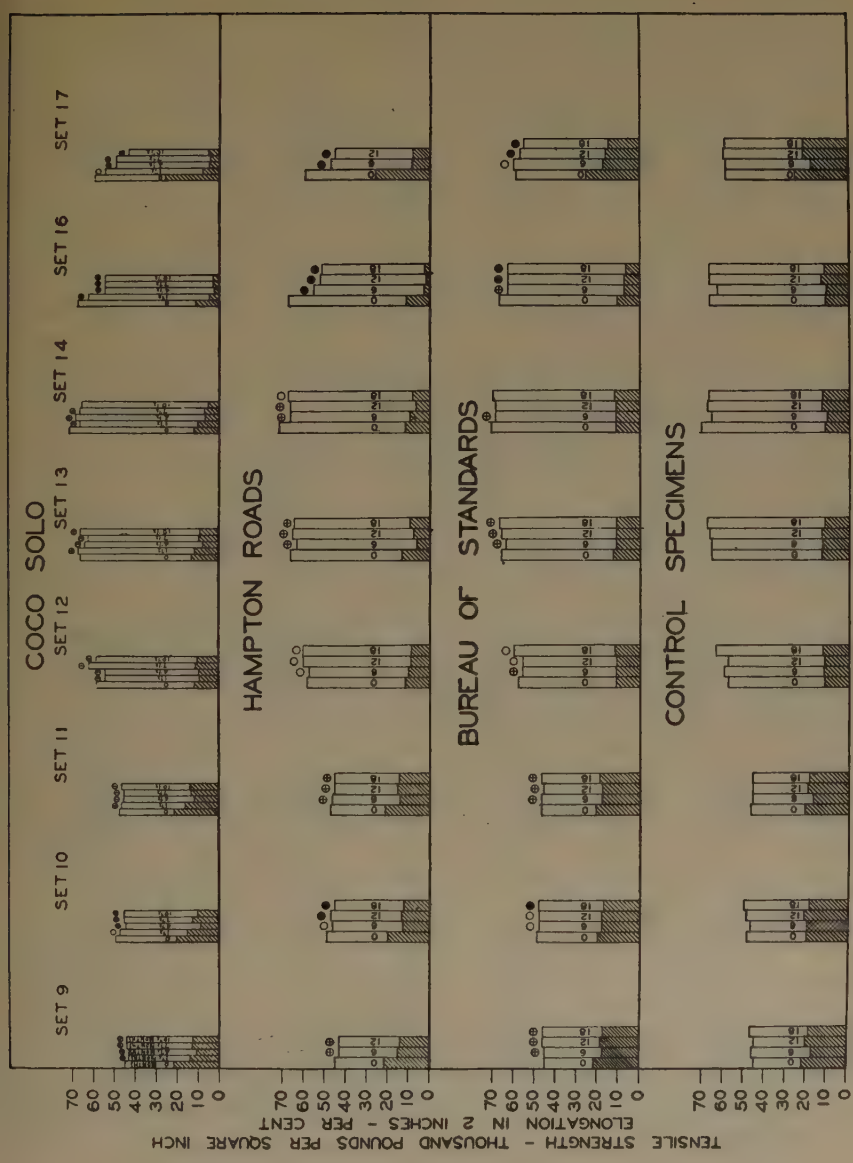


FIG. 7. (CONTINUED).—SUMMARY OF RESULTS OF TESTS OF SPECIMENS OF SAME MATERIALS EXPOSED TO WEATHER IN THREE LOCATIONS AND OF "CONTROL" SPECIMENS. REFER TO TABLE 2 FOR TREATMENT OF MATERIAL PRIOR TO EXPOSURE.

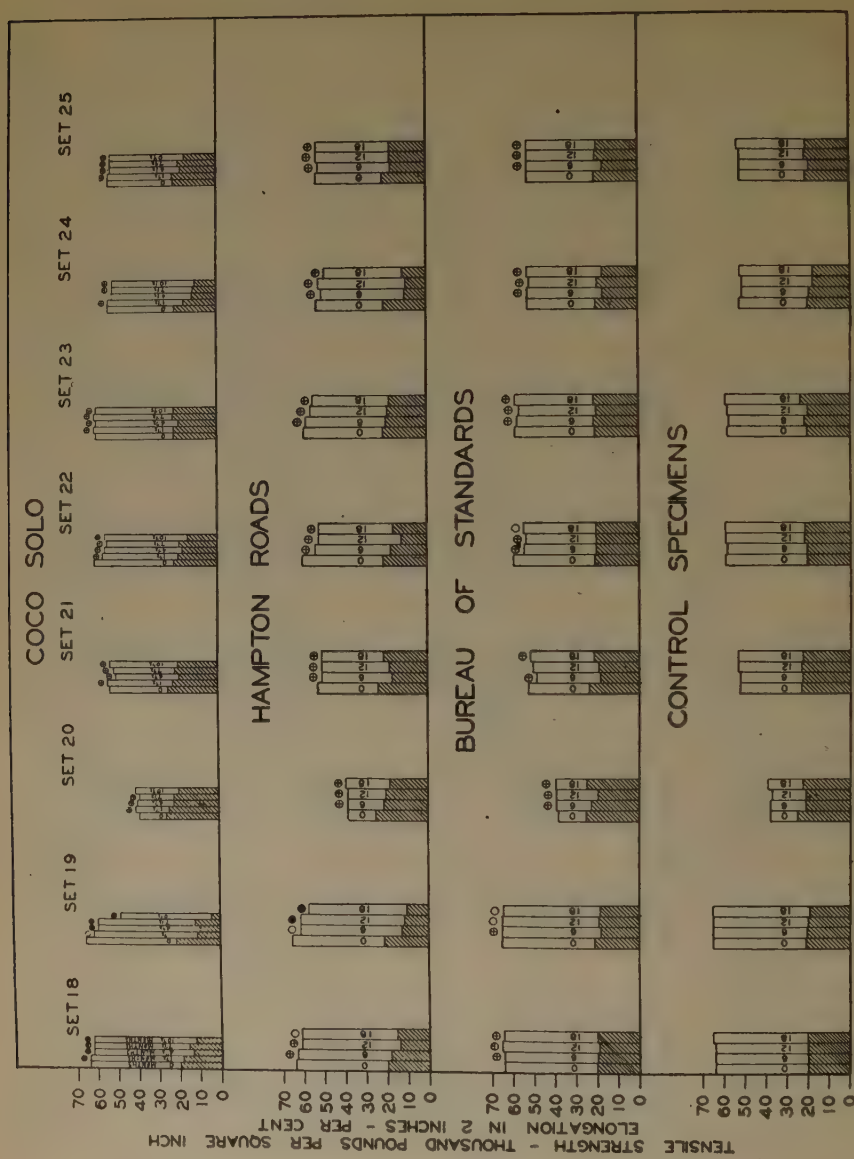


FIG. 7. (CONTINUED).—SUMMARY OF RESULTS OF TESTS OF SPECIMENS OF SAME MATERIALS EXPOSED TO WEATHER IN THREE LOCATIONS AND OF "CONTROL" SPECIMENS. REFER TO TABLE 2 FOR TREATMENT OF MATERIAL PRIOR TO EXPOSURE.

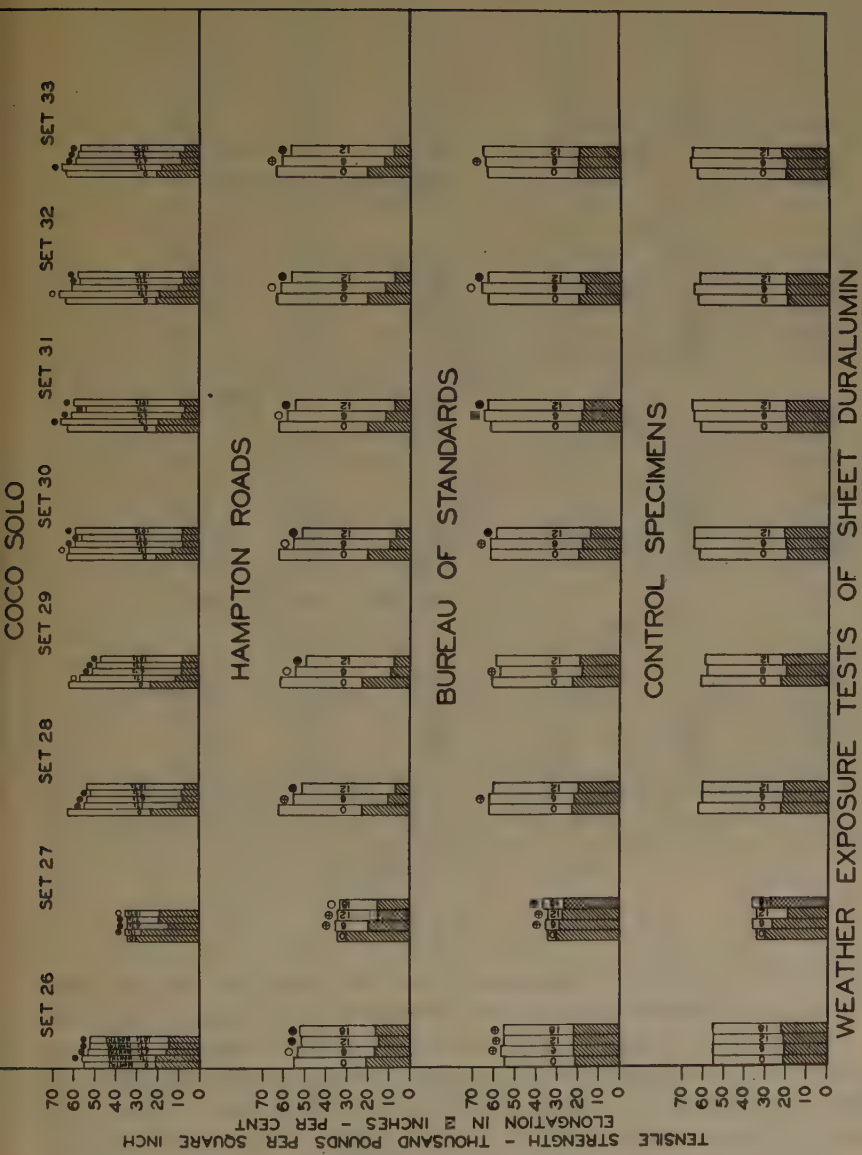


FIG. 7. (CONTINUED).—SUMMARY OF RESULTS OF TESTS OF SPECIMENS OF SAME MATERIALS EXPOSED TO WEATHER IN THREE LOCATIONS AND OF "CONTROL" SPECIMENS. REFER TO TABLE 2 FOR TREATMENT OF MATERIAL PRIOR TO EXPOSURE.

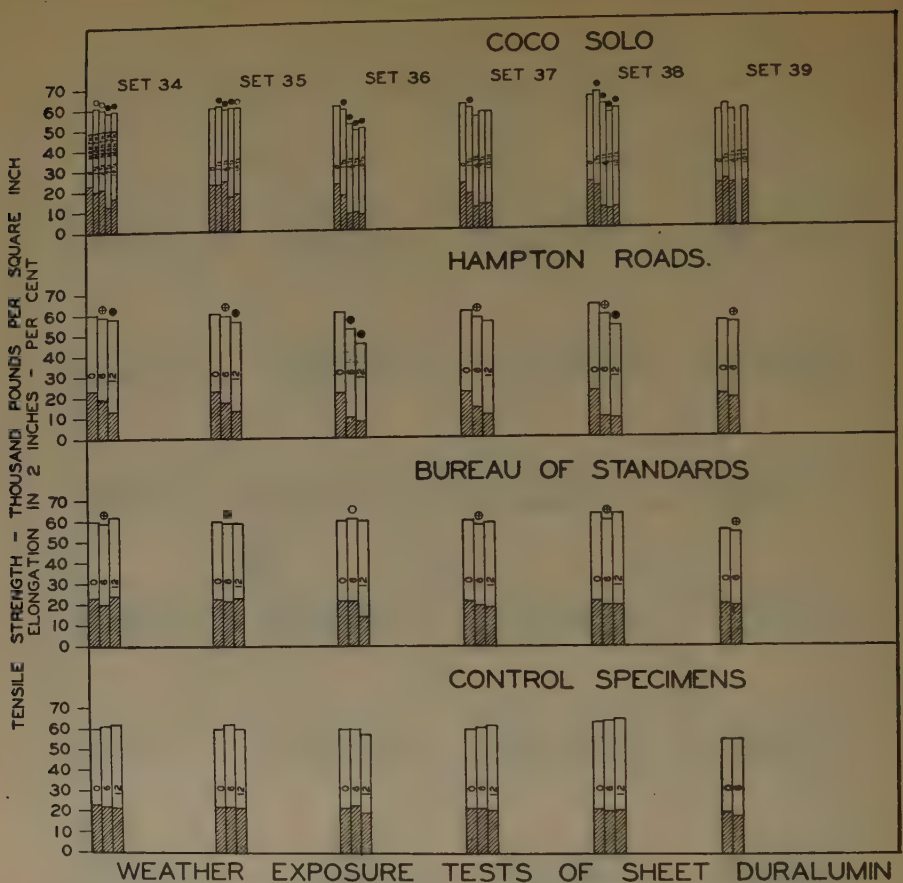


FIG. 7. (CONTINUED).—SUMMARY OF RESULTS OF TESTS OF SPECIMENS OF SAME MATERIALS EXPOSED TO WEATHER IN THREE LOCATIONS AND OF "CONTROL" SPECIMENS. REFER TO TABLE 2 FOR TREATMENT OF MATERIAL PRIOR TO EXPOSURE.

DISCUSSION

The results of the exposure tests have definitely shown that sheet duralumin is not permanent under atmospheric exposure under all conditions. As a general rule, no noticeable or significant changes have been noted in the properties of duralumin when maintained under conditions such as render the chance of the occurrence of corrosion very remote. The conclusion that the impairment of the material which occurs is the result of corrosion is believed to be fully warranted. Those cases in which deterioration of the material under atmospheric exposure occurs, very closely parallel the corresponding cases in the laboratory corrosion tests. The variations noted in the intensity of the attack under atmospheric exposure according to climatic conditions are in good accord with predictions based upon the laboratory tests. Exposure to

marine atmospheric conditions is decidedly more effective in producing intercrystalline corrosion than exposure to inland atmospheres. Likewise, other conditions being the same, a warm climate is more severe than a colder one.

The susceptibility of sheet duralumin to corrosive attack by the intercrystalline method was found to be intimately related to the method employed in the heat treatment of the material, in both the exposure and accelerated corrosion tests. The agreement as to the character of the results in the two cases is exceptionally good (Fig. 7, sets 1 to 4 and 7 to 8). Without question, the use of hot water or oil as a quenching medium for the heat treatment of sheet duralumin is not to be recommended for material which must withstand severe weather conditions, despite the fact that the tensile properties of duralumin do not differ noticeably according to the different quenching media used. It will also be noted from Fig. 7, that those materials which, after quenching, were aged at an elevated temperature, for example, sets 6 and 36, or which were heated somewhat after being allowed to age fully at room temperature (set 17) are decidedly susceptible to intercrystalline corrosion. On the other hand, it should be noted that corrosion of the more familiar pitting type frequently occurred on materials which had been heat-treated by approved methods, the drop in the tensile properties, especially elongation, accompanying this type of corrosion being quite marked in some cases (for example, set 2).

Of the different variables in heat treatment, the subsequent behavior of sheet duralumin is affected most by the quenching rate and the aging treatment. The exposure-test results have shown no difference in corrosion resistance resulting from varying the heating period prior to quenching. The results for sets 4 and 5 (Fig. 7) show no difference in the corrosion behavior of duralumin sheet heated for 15 or for 60 min. at 500° C. (920° F.) prior to quenching.

If duralumin is quenched from a temperature somewhat below that at which the alloy constituents pass completely into the solid solution condition, the tensile properties are not so high as may be developed by using a higher quenching temperature. The corrosion resistance may also be less as shown by set 10 (Fig. 7).

Cold working of fully heat-treated sheet duralumin did not render the material noticeably prone to intercrystalline attack in the atmosphere (sets 12, 13 and 14). This was true regardless of whether the cold-worked condition was a local one, such as produced by stretching the central portion or reduced section 10 per cent., or a more uniform cold-worked condition produced by cold rolling the entire bar sufficiently to increase its length 10 per cent. However, in the case when the material was not properly heat-treated, cold working by stretching accentuated the embrittling intercrystalline attack (set 16).

Variations in the composition of duralumin of the magnitude indicated in Table 2 are of minor importance so far as the resistance of the material to intercrystalline attack is concerned (sets 20 to 25). The "initial" tensile properties of most of these alloys are considerably lower than those of the ordinary duralumin after heat treatment and are less suitable for this reason. Corrosion by pitting, however, in some seemed to be accentuated, for example set 24 of relatively high iron content seems to be prone to this form of attack. No essential difference has been found to exist in the sheet duralumin made by different manufacturers if heat-treated in the same manner (compare BT materials with the others in Fig. 7), although the composition often differs somewhat. Of the two alloys which differ markedly from the "duralumin composition," the one containing copper, alloy 25S (set 26) has shown marked intercrystalline attack, whereas in alloy 51S (set 27) which contains no copper, only traces of intercrystalline attack were found after prolonged exposure to severe weather conditions.

The lack of permanence under exposure to the weather of most of the coatings used (sets 28 to 39, Fig. 7) is in good agreement with the indications of the laboratory tests. The use of duralumin which had been heat-treated by quenching in hot water and, hence, quite susceptible to intercrystalline attack as a basis material for the application of the coatings has proved very satisfactory. An earlier series of exposure tests of a somewhat preliminary nature had shown the desirability of this, since if the duralumin sheet in its uncoated state has a high degree of resistance to corrosion, no conclusions concerning the real protective value of the coatings other than qualitative ones based upon visual inspection can be drawn.

The conclusion, based on the laboratory results, that of the various coatings, a surface layer of aluminum is by far the most dependable has been borne out by the exposure tests on the aluminumclad sheet. As is shown by set 37 (Fig. 7), however, an aluminum-pigmented varnish may give excellent results under some conditions. That this is not always so, however, is shown by set 28 (Fig. 7).

Coatings consisting of a surface oxide film produced by the "anodic process" (set 32) or closely related coatings formed by chemical means (set 30) are undependable. The application of grease to such coatings at the outset, without subsequent renewal of the grease, has not materially increased the protection afforded by such coatings over the period covered by the tests (12 months). Likewise the use of a grease coating applied by rubbing and which is then "bonded" by the application of aluminum powder, has not proved entirely dependable for the entire period during which the tests have been in progress. It is of interest to note, however, that for the relatively mild weather conditions obtaining in Washington and on the basis of which one might expect to draw nicer distinctions as to

the merits of the coatings, the clear varnish and the "oxide" types of coatings have proved noticeably inferior to all of the others used.

In one important instance the weather-exposure tests have not corroborated the laboratory tests. A rubberlike coating (thermoprene) pigmented with aluminum powder gave excellent protection against corrosion to duralumin in rather severe conditions in the laboratory. The difference observed when exposed to the weather is most probably to be attributed to a deterioration of the matrix of the coating which occurs despite the aluminum pigment added to prevent this. (The results for this type of coating are not given in Fig. 7.)

In one rather important respect, weather-exposure tests of the kind described in this report may not duplicate service conditions. Most aircraft parts, in service, are always in a more or less stressed condition. Service tests to show the effect of stress on the corrosion behavior of duralumin parts are practically impossible. Laboratory tests on this point, however, are in progress. In brief, the tests consist in showing to what extent the tensile properties of sheet duralumin are affected by corrosion when the metal is under stress. Two general cases are being considered: (*a*) simple or "static" tension, and (*b*) repeated flexural stress, the corrosive attack being carried out in the same kind of solution and by the same wet-and-dry corrosion method (repeated immersions at 15-min. intervals) as in the laboratory tests already carried out. The results of these "stress-corrosion" tests will form the basis of a later report. On the basis of the close parallelism which has already been found to exist between the results of the exposure tests and the laboratory corrosion tests of sheet duralumin, it is confidently expected that any pronounced change in the results of the laboratory tests resulting from the introduction of the variable of stress will be indicative of a corresponding behavior of the material under service conditions.

Summary

1. In a series of weather-exposure tests of sheet duralumin upon which accelerated corrosion tests in the laboratory by the wet-and-dry corrosion method in a sodium chloride solution had already been carried out, a close parallelism between the results of the two kinds of tests was found to exist. Predictions based upon the results of the laboratory tests were, with but few exceptions, fulfilled in the exposure tests. In cases of disagreement in such tests, the results of the exposure tests are always accepted.

2. It has been shown by these tests that the lack of permanence or embrittlement of sheet duralumin which has been observed in some of this material in service under some conditions is largely, if not entirely, to be ascribed to corrosion. A corrosive attack of an intercrystalline nature is

very largely responsible for the degree of embrittlement produced. In the exposure tests, as previously indicated by the laboratory tests, the rate of embrittlement was greatly accelerated by a marine atmosphere and by a tropical climate.

3. The tests, both in the laboratory and in the field, were carried out upon full-size tension bars, the change in the tensile properties being used as a measure of the effect of corrosion. This method is, by far, the best in cases like the present in which the tensile properties of the material undergo material change without corresponding change in surface appearance.

4. The exposure tests confirmed the laboratory tests in showing that variations in composition of duralumin which do not result in wide departure from the ordinary "duralumin composition" are of almost negligible importance so far as corrosion behavior is concerned. Of the high-strength aluminum alloys which differ materially in composition from duralumin, the alloy containing copper as the principal alloying element was most susceptible to intercrystalline attack.

5. Variations in the heat-treatment procedure used for duralumin appear to be major factors in determining the susceptibility of the heat-treated sheet to intercrystalline corrosive attack during exposure to the weather and likewise in accelerated corrosion tests. The quenching rate, as determined by the use of cold or hot water or oil as quenching media, and the aging treatment (room-temperature aging *vs.* accelerated aging) are the most important factors in this respect. The use of hot water or oil as a quenching medium for sheet duralumin or an accelerated aging treatment is not to be recommended for duralumin which must withstand severe climatic conditions, such as marine and tropical service.

6. Cold working of properly heat-treated sheet duralumin by stretching or cold rolling does not affect very greatly the susceptibility of the material to embrittlement by intercrystalline attack when exposed to the weather. With improperly heat-treated duralumin this factor is of much more importance.

7. The exposure tests have clearly shown that corrosion of the more familiar or pitting type may occur with duralumin. The effect upon the tensile properties although similar in character is, in most cases, decidedly less than that of the intercrystalline type. So far it has not been possible to correlate definitely the tendency of the alloy toward this form of corrosive attack with any condition of the material resulting from any particular heat treatment or other condition.

8. The determination of the permanence of coatings on duralumin under corrosive conditions, both in the laboratory and when exposed to the weather, has been most successfully done by applying the coating to tension bars of duralumin which had been improperly heat-treated and were, hence, quite susceptible to attack. The relatively rapid attack of

the underlying or basis metal following the "breakdown" of the coating was shown in the tension tests of such specimens after exposure.

9. In this way, it has been shown that aluminum coatings are, by far, the most dependable. The useful life of clear varnishes is very short, the addition of aluminum "pigment" increases the permanence of the varnish very greatly. On the other hand, the addition of aluminum pigment to rubberlike coatings while decidedly successful in the laboratory, under exposure conditions has not given satisfactory results. Surface oxidation by "anodic" process and similar coatings have no lasting protective value unless well greased, and even when greased they have not proved to be resistant against severe exposure conditions, although with milder exposure conditions fairly satisfactory results have been obtained. Simple grease coatings "reinforced" with aluminum powder have given satisfactory service under mild exposure conditions but not entirely so for severe (marine) conditions.

10. Weather-exposure tests of the kind described here, while closely approximating service conditions, undoubtedly do not duplicate them. Tests are now in progress for the purpose of showing how the corrosion behavior of sheet duralumin may be affected by a stressed condition coincident with the corrosive attack. However, the difference in the rate of attack of the material exposed to the weather in Washington and of similar material exposed to marine atmospheric conditions is so clear and the lack of permanence of most of the coatings used so unmistakable that definite conclusions concerning the conditions which underlie the lack of permanence of duralumin and the protective measures which must be employed are believed to be fully warranted on the basis of the results of these exposure tests.

DISCUSSION

E. H. Dix, Jr., New Kensington, Pa.—This paper is most encouraging to those who are working on corrosion problems. The success of the correlation of laboratory tests with service exposure tests which Mr. Rawdon has achieved in this work may be attributed primarily to the method used in evaluating the effect of corrosion; *i. e.*, the change in the tensile properties, and the very thorough knowledge of the whole problem which has been displayed by Mr. Rawdon.

If there is any criticism that can be applied to this particular group of tests, it is that one specimen only has been tested for each period and location. There are sufficient periods and locations so that this will not interfere with the general conclusion, but it may make some individual results difficult to explain; that is, there is generally a variation in results of tests on individual specimens, so that in studying these charts it will, perhaps, be well not to pay too much attention to small variations shown from one period to another. For example, at times there is an increase in tensile strength and elongation after a few months' exposure.

We have been working on this problem for some years. Our general mode of attack has been very similar to that described by Mr. Rawdon. Within the last month we have received our own outdoor exposure results for an exposure period of

one year, and have been greatly encouraged by the close check between the service exposure and the earlier laboratory tests.

In the laboratory tests we have used both the alternate immersion test described by Mr. Rawdon, in which salt water with the addition of a small amount of hydrogen peroxide is used as the corrosion medium, and the salt-spray test. This alternate immersion test is very quick; the salt-spray test is slower. For instance, 48 hr. in the alternate immersion test gives about the same loss in properties as would be obtained in about three or four months in the salt-spray test.

We had previously found that the alternate immersion tests were checked very closely by the salt-spray tests, and now we are finding that the service tests are checking these accelerated corrosion tests, which is very gratifying, particularly after we have heard so much against the use of salt-spray tests.

We who are working with aluminum alloys are particularly fortunate in being able to use the salt-spray test, because it represents perhaps the most severe atmospheric condition to which the aluminum alloys are subjected in service.

In the first part of his paper, Mr. Rawdon states that the presence of copper is the chief cause of the intergranular corrosion. I feel that we should take exception to this and state the question more broadly. I think Mr. Rawdon will agree that we can say that the intergranular corrosion of the strong aluminum alloys is associated with any form of alloy and heat treatment which causes a precipitation, and as you know this is a submicroscopic precipitation.

It does happen that one alloy containing principally copper is more severely attacked in this manner than the straight duralumin. On the other hand, if a small amount of silicon is added to duralumin and artificial aging is applied, that is, aging at elevated temperatures, the corrosion is still more marked. As a further illustration: last year we heard, from Dr. Guertler, of an aluminum alloy containing the compound $MgZn_2$ and we now know that this alloy is very susceptible to intergranular attack, although it contains no copper.

I am interested in conclusion 3, which states that cold working of sheet duralumin has practically no effect on its corrosion resistance. I think we can go a little further in some cases. We have found that a certain amount of cold rolling after heat treatment has a tendency to increase the corrosion resistance. I think this may be accounted for by the breaking down of the surface grains, thus destroying the crystalline boundaries which act as pathways for the corrosion to follow.

In general we agree with Mr. Rawdon that oxidized coatings alone have little protection effect, but our own tests have shown that as a basis for paint they are good. Whether they are good because they are porous, and so allow the paint to adhere, or whether their benefit comes from corrosion protection afforded the surface of the aluminum, so that when moisture penetrates the paint film there is no incipient corrosion to blister the paint, we do not know.

We confirm the fact that the anodic process is not a protection unless the grease is frequently applied. We have had tests exposed on the roof of our building at New Kensington for only three months where the anodic coating with grease has been found to be without an appreciable protective effect.

In conclusion 11, Mr. Rawdon says: "Metallic aluminum coatings produced either by the metal-spraying process or by rolling a duplex slab having duralumin core and aluminum surface into sheet form, thereby producing a coating which forms an integral part of the finished sheet, have given most excellent results. Protection of the "cut" edges of aluminum-coated duralumin sheets appears not to be necessary if the sheet has been properly heat-treated."

This protection applies not only to the "cut" edges, but to the much larger areas. I think there is no doubt now that this is an electrolytic protection. The solution potential of the high-purity aluminum is enough greater than that of the alloy, which

contains 94 per cent. aluminum, to make this electrolytic protection effective. It not only absolutely protects the sheared edges, but it also protects normal duralumin rivets used in this sheet.

We have removed the surface over an area 1 in. dia. and found the protection absolute. However, there is abundant evidence of electrolytic action, because surrounding these areas the pure aluminum has been dissolved to a marked extent. In the commercial product produced under the name of Alclad sheet there is a diffusion zone between the strong alloy and the pure metal, and so evidently there are three solution potentials to be considered: that of the pure metal, of the diffusion zone, and of the alloy. Consequently pitting extends only to the diffusion zone. Then the diffusion zone is protected by the surrounding pure aluminum. This effect is of interest in studying the specimens visually because such solution of the coating presents a bad appearance even though the strength and ductility have not been affected. I agree with Mr. Rawdon that visual inspection and also the loss in weight means little in connection with the study of aluminum alloys.

The effect of the higher solution potential of the pure aluminum leads us to believe that the mechanism of intergranular corrosion is associated with the difference between the solution potential of the relatively high-purity metal at the grain boundaries and that of the matrix of the grains containing the submicroscopic precipitate. I am afraid the time is too short to go into that.

I want to add just one thing, and that is that we are here studying corrosion of sheet. Corrosion of thin sheet is important, but do not let us attempt to carry these results into the heavier sections where the effect of corrosion is relatively much less

H. S. Rawdon.—It is gratifying to know that the work of Mr. Dix is confirming our work, and that the two are going along so nicely together. I like to think of these tests as "pilot tests," as Dr. Gillett usually calls them. We do not claim that any test of only one specimen begins to tell the whole story; such a test, however, usually serves to point the direction along which we should proceed, and I think that "pilot test" is a very good name to apply to such tests.

Inhibition of Corrosion of Aluminum by Soaps

By H. V. Churchill,* New Kensington, Pa.

(New York Meeting, February, 1929)

There are two distinct methods of combating corrosive conditions. The first and most popular method is to choose a surface or material which will give adequate service under the specific and general conditions which are present. The second is a control or modification of the corrosive conditions to the end that metals and materials which would be attacked and corroded without such control or modification may be used.

Under the first method of attack of the corrosion problem may be grouped such devices as the selection of metals or alloys which offer great resistance or the use of protective coatings such as paints, lacquers or metallic coatings. Such procedures are exceedingly useful. It is undoubtedly true that most of the problems of corrosion will be solved by recourse to this first method of attack.

However, it must be remembered that there are many conditions in which metals are used where the choice of the particular metal to be used must depend upon other factors than corrosion behavior. Some of the factors which may govern the selection of metals for specific use are the physical and mechanical properties of the metals. But there is another factor which is of prime importance and that is relative price.

It is the pressure of these factors of mechanical properties, physical characteristics, and relative price that has acted as the stimulus for the second method of combating corrosion. The producer and user of various metals is confronted with the fact that because of mechanical properties, physical characteristics, or price, the use of a particular metal is desirable even though the corrosion conditions are adverse to the use of the metal. In many cases, the successful use of the metal may be made even though it is impossible to protect the metal by coatings. This is rendered possible by control or modification of the corrosive media.

Use of Sodium Silicate to Prevent Attack by Alkali Solutions

This idea of controlling or modifying corrosive media is well illustrated by some recent experiences with aluminum. For a number of years collapsible tubes have been made of aluminum. Due to the ease with which aluminum is attacked by even mild alkalies, the use of such tubes

* Research Bureau, Aluminum Co. of America.

has been confined to the packing of neutral materials. Since the alkalinity of most materials packed in collapsible tubes is due to the hydrolysis of the soaps used and is small in amount, it was thought that the problem might be solved. The behavior in aluminum tubes of such materials as shaving creams which are mild soaps is quite interesting. When most shaving creams are packed in aluminum the first evidence of action is a swelling of the tube resulting from the pressure of the hydrogen evolved incident to attack on the aluminum tube by the alkali in the soap or cream. Soon the tube wall is penetrated and under interior pressure the tube contents exude through the holes thus produced. Examination of the interior of the tube shows general etching over the surface.

It has been known for some time that suitable proportions of sodium silicate added to sodium carbonate solutions would prevent attack on aluminum immersed in such solutions.[1] This is readily demonstrated by immersing a piece of aluminum in a boiling solution of sodium carbonate (150 g. Na_2CO_3 per l.); hydrogen is copiously evolved. If to this solution, sodium silicate be added drop by drop, the visible evolution of hydrogen will stop and further attack on the aluminum will be prevented.

Contrary to the opinion of some authorities, it has been our experience that sodium silicate has but little effect on the attack on aluminum by such materials as sodium or potassium hydroxide except in rather low concentrations of hydroxide. It appeared that the inhibition of attack by sodium carbonate was to some extent due to the presence of the carbonate ion. The inhibitive action of sodium silicate on other readily hydrolyzed materials which attack aluminum, such as sodium borate and sodium phosphate, was tested. Inhibition was produced in all cases.

Different proportions of sodium silicate were then thoroughly mixed with various shaving creams. The resultant products were packed in aluminum tubes and held for 30 days before examination. Control tubes of the creams without the silicate were run in parallel with all tests. Examination of the tubes revealed that inhibition had been effected in practically all cases where silicate was used.

Later it was determined that effective inhibition could be effected by adding to a shaving cream 0.20 per cent. by weight of sodium silicate solution. Creams which without silicate seriously etched and penetrated the tubes, showed absolutely no attack when sodium silicate was incorporated to the extent of 0.20 per cent.

Mechanism of Inhibition Phenomena

This experience with soaps, coupled with somewhat similar experience with carbonates, borates and phosphates, and very dilute hydroxide

[1] R. Seligman: Milk and Metals. *Proc.* World's Dairy Congress (1923) **2**, 1202.

solutions raises the interesting question of the mechanism of the inhibition phenomenon. It seems that two theories may be advanced to explain the action. One theory holds that there is deposited on the surface of the metal a thin film of silica or silicate which mechanically prevents the corrosive alkaline materials from actually coming into contact with the metal. Corollary to the theory as thus expressed is the idea that this thin film is an impervious mixture of silica and hydrated aluminum oxide. There is no actual visible evidence that any film actually is present on the aluminum. However, it is true that better and more effective inhibition is secured when silicates of higher silica to soda ratios are used thus making more silica available for film forming. There is yet other evidence available that the aluminum may be protected from alkali produced by hydrolysis by means of films. The corrosion of aluminum by such materials as sodium carbonate, sodium phosphate and soaps may be greatly reduced and in many cases absolutely prevented by means of small additions of potassium dichromate to the corroding media. For example, if to most shaving creams you add potassium dichromate in the proportions of 4 mg. dichromate to 20 g. cream the resultant material will not corrode aluminum. It is difficult to predicate this protection on any other basis than the formation or maintenance of a protective film. In passing it may be said that dichromate also adequately protects aluminum against corrosion by many industrial and saline waters.[2]

The other theory which has been advanced to explain how the silicate functions in protecting aluminum from attack by alkalis produced by hydrolysis is somewhat vague. Nevertheless, it presents some points of interest. The theory is that the silica in sodium silicate and hence the silica in soaps to which sodium silicate has been added is present in colloidal form. Being in colloidal form it possesses certain characteristics that enable it to combine with or hold to the alkali produced by hydrolysis in such a way that it is not available for reaction with the aluminum. Since as noted above, an increase in the ratio of silica to soda in the silicate added results in more effective inhibition, it may be that more effective inhibition is due not to the fact that more silica is available for film-forming purposes but that more silica is available to hold inactive the alkali produced by hydrolysis. Another bit of information that may have some bearing on the matter is the fact, which is known to many soap chemists, that the addition of sodium silicate to soap of definite hydrogen ion concentration lowers the pH, that is, brings it nearer to the neutral point.

In the absence of sufficient information, we cannot definitely establish the correctness of either theory and rest on the empirical fact that effec-

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[2] R. Seligman and P. Williams: The Action on Aluminum of Hard Industrial Waters. *Jnl.* Inst. of Metals (1920) **23**, 171.

tive inhibition of corrosion of aluminum by soft soaps may be effected by adding sodium silicate to the soap.

The delicate balance that exists between conditions that cause and promote corrosion and those in which there is no corrosion is illustrated by the work recited in this paper. To cope successfully with corrosion no weapons must or can be spared. There is some remedy for all corrosion; sometimes it lies in the proper choice of material, sometimes in adequate coating and sometimes in control or modification of media.

DISCUSSION

F. N. Speller, Pittsburgh, Pa.—Sodium silicate is quite commonly used, not only for the prevention of corrosion of iron but also for the protection of lead.

Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids

By Norman B. Pilling* and Donald E. Ackerman,* Bayonne, N. J.

(New York Meeting, February, 1929)

Summary

The solubilities of a series of experimental alloys covering the range 0 to 100 per cent. Ni, 0 to 30 per cent. Cr have been studied under conditions of complete submersion in several fully aerated acid solutions, and in solutions containing sulfurous acid. In nonoxidizing, hydrogen-discharging acids, if the nickel content is below a certain critical amount, chromium increases the rate of solution and nickel decreases this rate; this critical content of nickel is about 13 per cent. Alloys containing more than this corrode at a constant minimum rate independent of iron, nickel or chromium contents. Austenitic chrome-nickel steels may thus have a resistance to these acids equal to that of nickel-chromium alloys. In nitric acid and in unaerated sulfurous acid rather sharp limits of attack occur which are principally dependent on chromium content. In the former the limit of attack is not related to a particular chromium content but varies continuously with acid concentration. The action of sulfurous acid on these alloys is highly dependent on the presence of small amounts of other substances in solution, and many sulfurous acid mixtures rapidly attack alloys to which the pure acid is wholly inert.

The observed effects are not compatible with Tammann's theory relating corrosion resistance to lattice structure but are believed to be concordant with current views of the electrochemical nature of corrosion.

Introduction

The discovery, development and engineering application of iron alloys resistant to corrosion may well claim a place among the important developments in metallurgy of the past two decades. The varied demands of industry coupled with the skill of the metallurgist have resulted in the production of an extensive group of steels and alloys ranging from the now familiar "stainless" chromium steels of the kitchen to special alloys of great chemical complexity for particular, exacting needs. Any adequate description of the important properties of these—physical, chemical and economic—would be a formidable undertaking.

* Research Laboratory, The International Nickel Co., Inc.

Systematically, if not historically, these alloys have as their foundation the ternary iron-nickel-chromium series, and the intention of the present paper is to discuss a few of the corrosion-resisting properties, under simplified conditions, of a portion of this group of alloys. Its subject matter, therefore, is a small and special portion of a large and important problem.

This field has received the attention of many previous investigators, whose results have not been entirely concordant. Much of this earlier work preceded the renewed activity regarding the mechanism of corrosion processes which, in the hands of McKay and others[1] during the past eight years, has shown that corrosion is with great probability essentially electrochemical in nature and hence conditions in the external environment are quite as important in determining rates of corrosion as those relating solely to the metal. The present tests were not designed to demonstrate these variables but to display the extent to which the corrosion resistance of the iron-nickel-chromium alloys is related to their composition. The tests have been conducted for the most part following a standardized technique, later described in detail, in which careful attention has been given to the control of temperature, agitation and aeration, and sufficient bulk of solution provided to minimize depletion effects during the progress of a test.

Some difficulty in the interpretation of data is due to the fact that observed corrosion rates may change continuously in the ratio of nearly one million to one, and the plotting of such data involving changes of magnitude of this order may lead to faulty conclusions if a uniform scale of corrosion rates is used. For example, if the corrosion rates of chromium steels in dilute nitric acid are plotted to such a uniform, arithmetic scale, it is entirely possible to reach the false conclusion that the rate becomes zero at about 12 per cent. chromium content; if the corrosion scale is logarithmic, all ranges of magnitude receive equal emphasis and it becomes apparent that the corrosion rate, although small, still changes continuously even at chromium contents higher than 12 per cent. Logarithmic plotting has therefore been used in representing the present data.

The passivity of iron produced by exposure to strong nitric acid is very familiar; Hatfield[2] was perhaps the first to show that chromium steels may acquire a degree of passivity by exposure to nitric acid sufficiently persistent to diminish greatly, if only temporarily, their solubility

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[1] R. J. McKay: Corrosion by Electrolyte Concentration Cells. *Trans.* Am. Electrochem. Soc. (1922) **41,** 201; The Common Occurrence of Corrosion by Electrolyte Concentration Cells. *Ind. & Eng. Chem.* (1925), **17,** 23.

U. R. Evans: Corrosion of Metals. 2d Ed. London, 1926. E. Arnold & Co.

[2] W. H. Hatfield: Corrosion as Affecting the Metals Used in the Mechanical Arts. *Engineer* (1922) **134,** 639.

in dilute sulfuric acid. We can confirm this not only for chromium steels but for many iron-nickel-chromium alloys, and have found that such passivity can also be induced even in sulfuric acid solutions by anodic discharge and removed by cathodic discharge. The greatest care is necessary at times in order to avoid bringing such alloys inadvertently, prior to test, into a passive condition which is often stubbornly persistent in many dilute acids.

Experimental Alloys

The alloys upon which the present tests were made comprised about 90 experimental melts covering, in varying degrees of density, the portion of the ternary diagram containing 30 per cent. chromium or less. This included:

1. A series of low-carbon chromium steels ranging from 0 to 32 per cent. Cr.

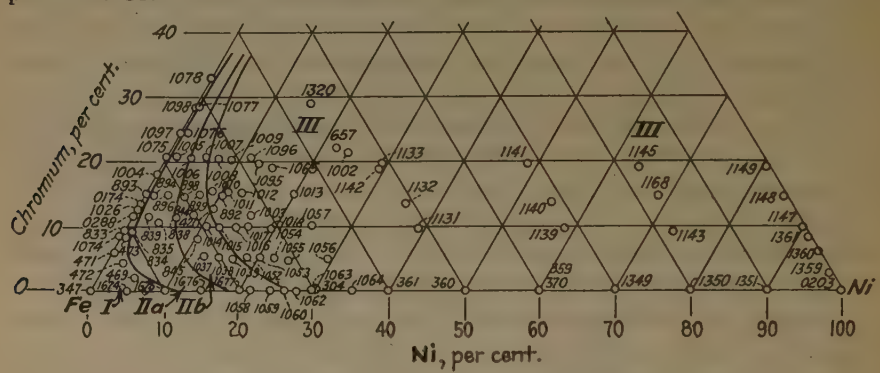

Fig. 1.—Index to experimental alloys.

2. Low-carbon nickel steels, ranging from 0 to 100 per cent. Ni.
3. Nickel-chromium alloys, 0 to 20 per cent. Cr.
4. Four groups of marginally austenitic nickel-chromium steels containing about 5, 10, 15 and 20 per cent. Cr, with nickel increasing in small increments from a concentration lying within the martensitic range to about 15 per cent. beyond it.
5. A number of iron-nickel-chromium alloys covering the range 10 to 20 per cent. Cr, 0 to 60 per cent. Fe.

An index to these is provided in Fig. 1.

All of these melts were made in an Ajax high-frequency furnace in magnesia-lined clay-graphite crucibles without slags or other protective coverings. The 4.5 kg. fusion was made of clean, electrolytic nickel (0.3 per cent. Co, < 0.1 per cent. other impurities), Armco iron and aluminothermically reduced low-carbon ferrochromium or chromium metal. No attempt was made to keep these alloys extremely pure, but on the contrary small additions of silicon (0.1 per cent.) and manganese

(0.3 to 0.6 per cent.) were made to insure soundness and malleability. We have generally found that the presence of these elements in the small quantities noted have far less effect on corrosion-resisting qualities than apparently minor changes in external test conditions.

These melts were cast into ingots 2¼ in. square, cropped, reduced about 80 per cent. in section by forging and annealed 30 min. at 1000° C., followed by furnace cooling. From these annealed forgings the corrosion test specimens in the form of disks were machined. Unless otherwise noted it may be assumed that this constituted the conditioning treatment of the alloys.

The iron-nickel-chromium alloys have some structural complexities, but for the present purpose it is sufficient to consider the portion of the series that contains less than 30 per cent. Cr as consisting, at room temperature, of three principal structural categories; *viz.*, I, pearlitic or ferritic, II, martensitic and III, austenitic "steels." The approximate limits of these fields in iron-nickel-chromium alloys of about 0.10 per cent. C content is indicated by curves in Fig. 1; the median line through the martensitic field marks where the γ lattice first appears, and the subfield marked II*b* thus denotes that group of martensitic alloys in which both the α and the γ lattice solid solutions occur. In the present paper the adjective "austenitic" is used loosely to refer to any γ lattice or nickel-like structure, whether of high iron content or not. As will become evident later, the acid solubilities of these alloys pay little attention to these structural distinctions, fundamental though they may be. Bain[3] has traced the approximate constitutional aspects of a portion of the series and has shown the existence of a low nickel-content phase (his *B* constituent) in high chromium-content alloys, which may be present in alloys containing more than 25 per cent. Cr with nickel greater than 5 per cent.

Technique of Corrosion Testing

The importance of the control of environmental factors has been briefly noted in an early paragraph. The art of corrosion testing is greatly indebted to the investigations of Thompson and McKay[4] who first demonstrated adequately the necessity for control of movement, aeration, etc., and devised a practical technique of testing embodying these essential factors. Their pioneer work has supplied that necessary degree of control which has made close reproducibility possible, and this is, of course, an essential requirement to any study like the present one.

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[3] E. C. Bain and W. E. Griffiths: Introduction to the Iron-chromium-nickel Alloys. *Trans.* (1927) **75**, 166.

[4] J. F. Thompson and R. J. McKay: Control of Motion and Aeration in Corrosion Tests. *Ind. & Eng. Chem.* (1923) **15**, 114.

With the exception of tests in sulfurous acid, and other instances specifically noted, the solubility tests were made in air-saturated, agitated solutions, the test piece wholly submerged and moving in a circular path in a vertical plane. The apparatus and set-up to accomplish this was of the Thompson-McKay type as further refined by Fraser, Ackerman and Sands, and reference is suggested to their paper[5] for its description in detail. The principal difference consisted in a modification of the aerating device, in which a glass chimney was substituted for a funnel, permitting more efficient aeration and agitation. The test conditions may be summarized:

Test specimen—Machined disk from forging, flat face normal to fiber of forging.
Size of specimen—About 1 in. dia. by $\frac{3}{16}$ in. thick.
Surface finish—No. 180 emery.
Mode of support—Glass stirrups.
Rate of motion—15.5 ft. per min.
Corroding solution: Concentration—5 per cent. by weight of reactant (also 35 per cent. HNO_3).
Temperature—30° C., thermostatically controlled.
Aeration—Saturated, with modified McKay aerator.
Volume—2 liters (1 specimen per cell).
Duration of Test—Usually 1, 3 or 20 hr.

After surfacing the specimens were washed with alcohol-ether and dried in a desiccator before weighing. At the conclusion of a test they were brushed to remove corrosion product, washed in water, dried, rinsed in alcohol-ether, dried in a desiccator and weighed.

Owing to the enormous differences in rate of solution encountered, it was not feasible to establish a fixed duration of test. This varied from 1 to 20 hr. depending on circumstances; except when hydrogen was discharged liberally, the duration of the test period had but a slight effect on the rate of corrosion measured. The results of corrosion are expressed as the weight loss in milligrams per square decimeter per day (abbreviated as Mdd.). This unit has the advantage of being of such size that minute decimals with many obscuring ciphers are avoided. For convenience, its equivalent in more homely units for alloys having a density of 8 to 9 is 1000 Mdd. = 0.17 in. pentration per year.

With the exception of steels of low nickel content, highly soluble in non oxidizing acids, the conditions of corrosion led to quite uniform attack without pitting. Check results within 10 per cent. of observed rates were generally expected and found.

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[5] O. B. J. Fraser, D. E. Ackerman and J. W. Sands: Controllable Variables in the Quantitative Study of the Submerged Corrosion of Metals. *Ind. & Eng. Chem.* (1927) **19**, 332.

Nitric Acid

Nitric acid is highly oxidizing and this property extends to its dilute solutions. Iron is rendered passive and insoluble by contact with this acid in concentrated form and chromium intensifies this propensity, in the sense that with high chromium contents passivity is attained with more dilute nitric acid concentrations. This valuable property of chromium steels and of iron-nickel-chromium alloys has been extensively exploited both in the manufacture and in the transport of nitric acid. Although under some conditions both chromium steels and the chromium alloys show almost complete resistance, this property does not hold for all conditions of temperature, concentration or the presence of other compounds in solution; dilute solutions such as 5 per cent. by weight, may corrode even alloys of high chromium content at surprisingly rapid rates. We have found that it is entirely possible for these alloys to exist and persist in either a passive or an active condition in dilute nitric acid. Among other conditions, the tendency toward passivity is greatly diminished if chlorides to the extent of 0.01 to 0.03 per cent. are present in the nitric acid solution.

Monypenny[6] has shown that the solubility of chromium steels in dilute nitric acid diminishes with time and ultimately reversion to complete passivity may occur spontaneously following solution at a high rate. He does not seem, however, to have shown that this is not a "depletion" effect characteristic only of his test method, as the powerful anodic polarization induced by the accumulation of iron salts in dilute nitric acid is well established.[7] A few tests of our own made in two liters of test solution, during the course of which the maximum metal accumulation amounted only to 0.05 per cent., gave no indication of such change in rate.

The data on solubility of the annealed alloys in 5 per cent. nitric acid are shown in Fig. 2. It is evident from this that dilute nitric acid solubility of the annealed alloys is almost entirely a function of their chromium contents, nickel having little effect. This figure shows eight series of alloys at eight different levels of iron content, from 0 to 100 per cent. The range of solubilities covered by chromium contents 0 to 30 per cent. is enormous, from 100 to nearly 500,000 milligrams per square decimeter per day.

The first 5 per cent. of chromium added to iron diminishes the nitric acid solubility rather slowly, but within the range 5 to 20 per cent. Cr, the solution rate drops rapidly, beyond this more slowly. It will be

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[6] J. G. H. Monypenny: Stainless Iron and Steel, 200. London, 1926. Chapman & Hall, Ltd.

[7] J. G. H. Monypenny: *Op. cit.*, 207.

noted that the logarithmic corrosion-rate scale shows that the action of chromium is continuous throughout this range and that no abrupt limit of attack occurs, such as will be shown later for several different acids.

The presence of nickel up to 30 or 35 per cent. increases perceptibly the solubility of steels containing more than 15 per cent. Cr. Beyond 35 per cent., nickel begins to diminish the solubility in dilute nitric acid in the absence of chromium and this has its effect on the ternary alloys

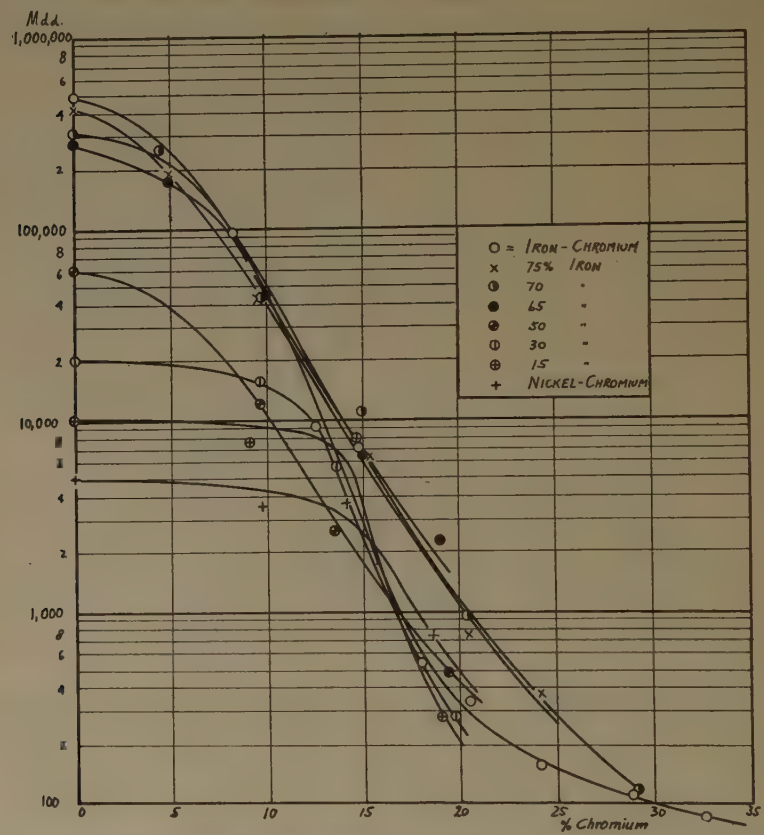

FIG. 2.—CORROSION RATES OF IRON-NICKEL-CHROMIUM ALLOYS IN 5 PER CENT. NITRIC ACID.

in that for chromium contents under 10 or 12 per cent., and iron contents between 70 and 40 per cent., the solubility for a given chromium content is lowered by replacing iron with nickel. This relation changes somewhat at lower iron contents and from 30 per cent. downwards the solubility of the lower chromium alloys is practically determined by the iron content. This holds only until a chromium content equivalent in solution rate to the particular iron content is reached, when higher chromium

contents depress the solubility almost identically with the chromium steels.

These relations, which seem involved when described, are quite clearly shown in Fig. 2.

With the exception of the chromium steels of Fig. 3 the data on 35 per cent. nitric acid have not been plotted. An inspection of the tabular

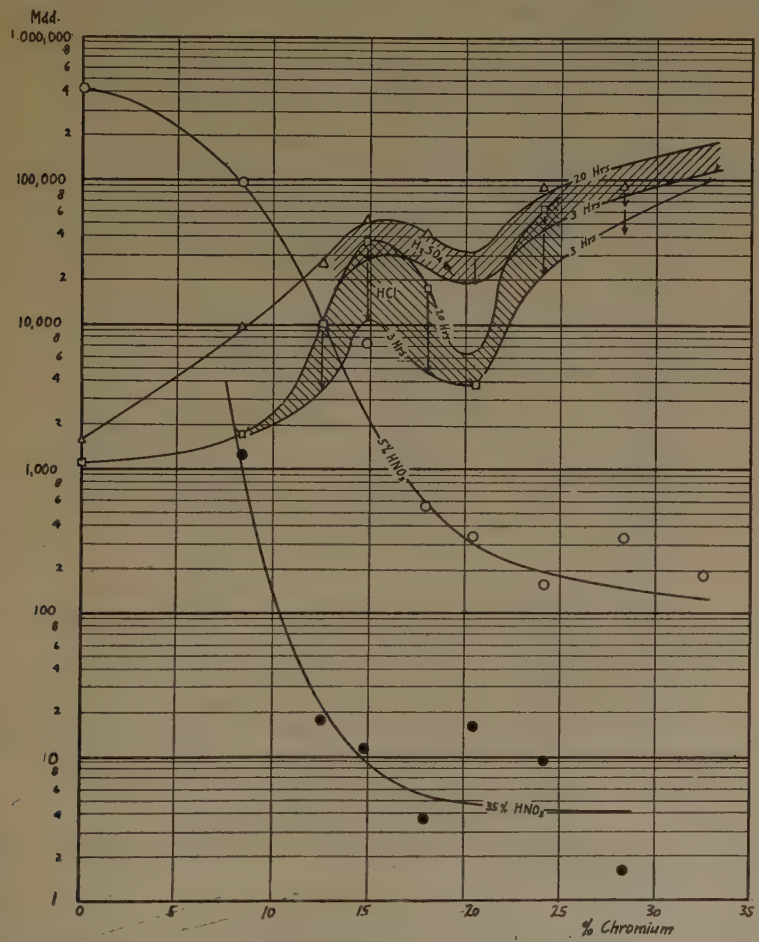

FIG. 3.—ACID SOLUBILITY OF CHROMIUM STEELS.

data in Table 6 shows that practically complete passivity is reached at above 5 per cent. Cr content.

The effect of nitric acid concentration on the chromium content of iron-chromium alloys at which passivity is induced is shown in Fig. 4. In these tests a weight loss of 5 mg. per sq. dm. or less in a 1-hr. test was taken as an arbitrary criterion of passivity. The relation between chromium content and nitric acid content is a continuous one, with no

indication that particular chromium contents have any special significance. The previously noted effect that nickel contents less than 30 per cent. increase the solubility in dilute nitric acid has its analog here, and an alloy containing 15.01 per cent. Cr, 13.01 per cent. Ni required a considerably higher acid concentration to acquire passivity than the chromium steel of equal chromium content.

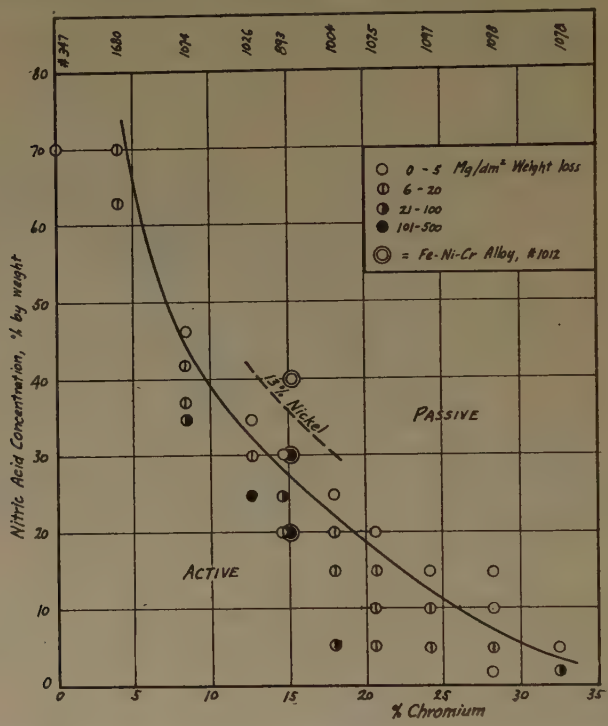

FIG. 4.—EFFECT OF CHROMIUM CONTENT ON PASSIVITY OF CHROMIUM STEELS IN NITRIC ACID.

HYDROGEN-DISCHARGING ACIDS

In this classification are included the nonoxidizing mineral acids and a great many organic acids.

Iron dissolves at a moderate rate in dilute sulfuric acid with the evolution of hydrogen, and the presence of chromium increases the solution rate greatly. This fact has long been known and is of historical interest as bearing the responsibility for a generation's delay in the recognition of the unique and valuable properties of high-chromium steels.[8]

As might be expected from the nature of the attack, increasing the concentration of sulfuric acid increases the solubility of the chromium steels (see Table 1).

[8] R. A. Hadfield: Alloys of Iron and Chromium. *Jnl.* Iron and Steel Inst. II-48 (1892).

TABLE 1.—*Steel Containing* 12.98 *Per Cent. Chromium,* 0.12 *Per Cent. Carbon*

20 Hr. at 30° C.

H_2SO_4, Per Cent.	Mdd.
10.9	12,000
17.7	30,000
26.9	40,300

It was found that the high-chromium steels, discharging hydrogen in gaseous form from solution, do not dissolve at fixed rates, but tend to increase in rate with time, to an extent which may treble the initially observed rate. This effect is of some importance in making comparisons between alloys differing in composition and in behavior; a typical example, which could be repeated for many other steels and acids, follows:

TABLE 2.—*Steel Containing* 24.1 *Per Cent. Chromium,* 1.2 *Per Cent. Nickel,* 0.21 *Per Cent. Carbon*

5 Per Cent. HCl, 30° C.

Time, Hr.	Mdd.
1	14,100
2	7,700
3	15,300
7	48,000
41	57,600

This acceleration in corrosion rate is accompanied by a marked roughening of the surface and it is believed that this, by lowering the hydrogen overvoltage, may be a responsible factor.

A résumé of the solubilities of annealed chromium steels containing 0 to 33 per cent. Cr is shown in Fig. 3. It is a curious fact that the increase in solubility with chromium content is by no means regular, but reaches a maximum at about 16 per cent. Cr. This is followed by a substantial decrease to a minimum at about 20 per cent. Cr, beyond which it again rises and is still increasing at the highest chromium content reached. In view of the variability of corrosion rate with time, this might be ascribed to accidental variations in control, but the several circumstances that these maxima and minima occur at the same chromium contents in both sulfuric and hydrochloric acids and are indicated equally well whether the high rates for a 20-hr. test period or the low rates for a 3-hr. test period are considered, leads us to consider this effect a real one. It is not of much practical significance, as the lowest rates in the region of the minimum at 20 per cent. Cr, of the order of 5000 Mdd,

are very rapid (about 25 times as fast as monel metal under the same test conditions).

It is convenient to consider the nickel-bearing alloys as divided into groups of approximately constant chromium contents. Five series are thus shown in Fig. 5, four of which contain nickel varying from 0 to 30 per cent.

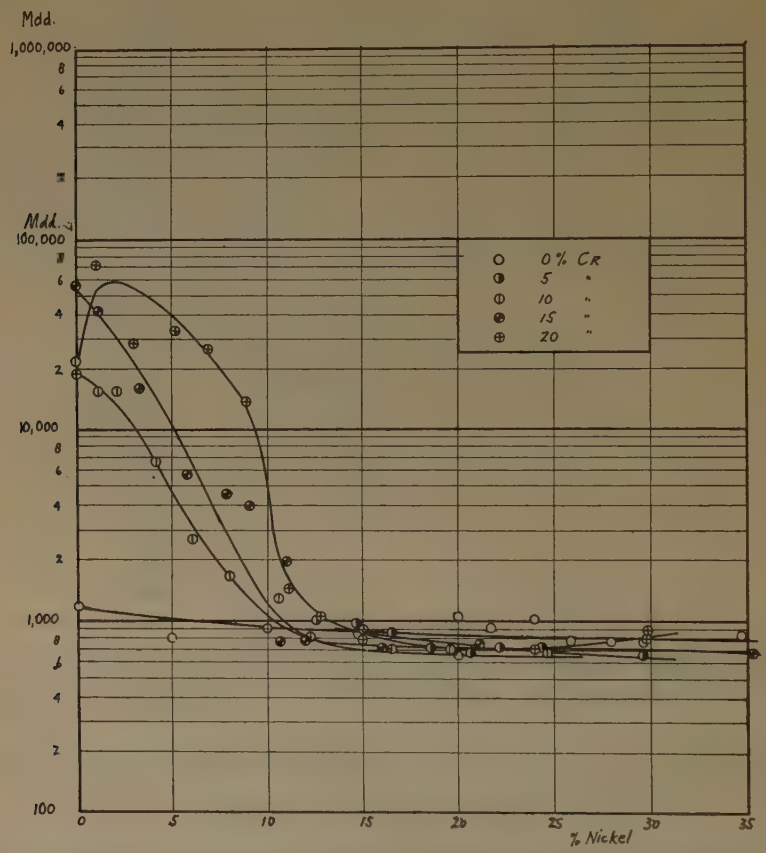

FIG. 5.—CORROSION RATES OF IRON-NICKEL-CHROMIUM ALLOYS IN 5 PER CENT. SULFURIC ACID.

Sulfuric Acid.—The effect of the first small additions of nickel to chromium steels depends somewhat on what the chromium content is. In the entire absence of chromium, the solubility of iron is reduced mildly by nickel. Steels with 10 or 15 per cent. Cr suffer an immediate diminution in solubility, 2 per cent. Ni about halving the corrosion rate. When chromium is around 20 per cent., corresponding to the minimum solubility in Fig. 3, the first addition of nickel brings about a rapid rise in solubility, and with more than 2 per cent. Ni these 20 per cent. Cr steels

all have sulfuric acid solubilities greater than those of lower chromium content. Expressed a little differently, the minimum solubility of the 18 to 22 per cent. Cr steels is rapidly wiped out by the addition of nickel and leads to no advantage in the nickel-chromium steels.

Increasing contents of nickel up to about 12 per cent. continue to diminish the solubility for all three chromium contents but this action suddenly ceases at about this nickel content, resulting in the rather remarkable condition that irrespective of chromium content, the maximum reduction in sulfuric acid solubility is completed with 12 to 15 per cent. Ni, at which nickel content the corrosion rate is depressed to

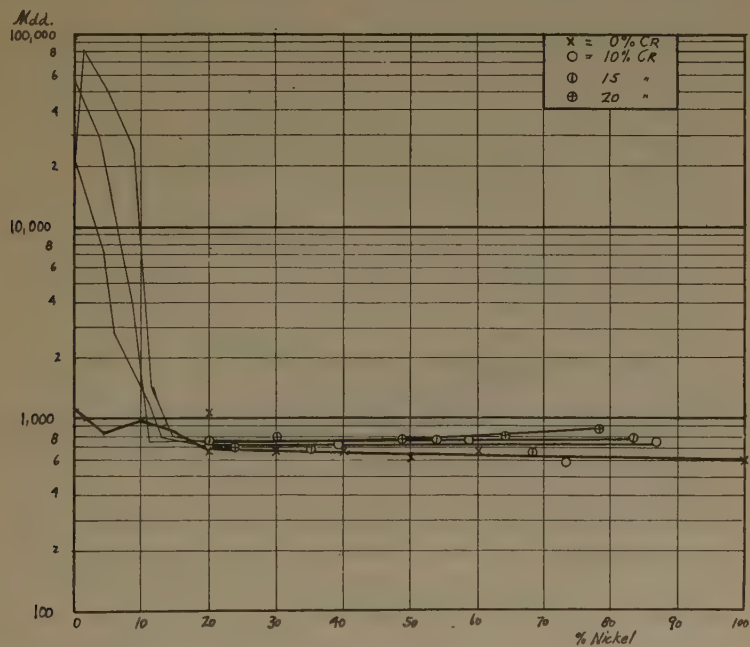

FIG. 6.—CORROSION RATES OF IRON-NICKEL-CHROMIUM ALLOYS IN 5 PER CENT. SULFURIC ACID.

a common level of 700 to 900 Mdd. This common corrosion rate is the same for all chromium contents between 0 and 20 per cent. However, if the chromium content is raised much above 20 per cent., in steels containing about 15 per cent. Ni, the alloy dissolves with evolution of hydrogen and shows a high corrosion rate; this rate is still much lower than that of the corresponding simple chromium steel. As an example, a steel containing 29.0 per cent. Cr, 15.2 per cent. Ni had a corrosion rate about 10 times greater than that observed with steels of lower chromium content but of the same nickel content. This behavior is thought to be due to the presence of Bain's *B* constituent in alloys of this type.

A broader view of this relation may be had in Fig. 6 in which the entire range of nickel contents is covered. The common level of corrosion rates occurring beyond the critical nickel content of 13 per cent. is maintained throughout; that is, no advantage results from increasing the nickel content far beyond the critical value.

Hydrochloric Acid.—In many respects hydrochloric acid and sulfuric acid are similar in their action upon the nickel-chromium steels (Figs. 7 and 8). Again, the addition of a little nickel to the 20 per cent. Cr steel increases its solubility greatly and further additions diminish the solution rate. The high solubility of the chromium steels (5000 to

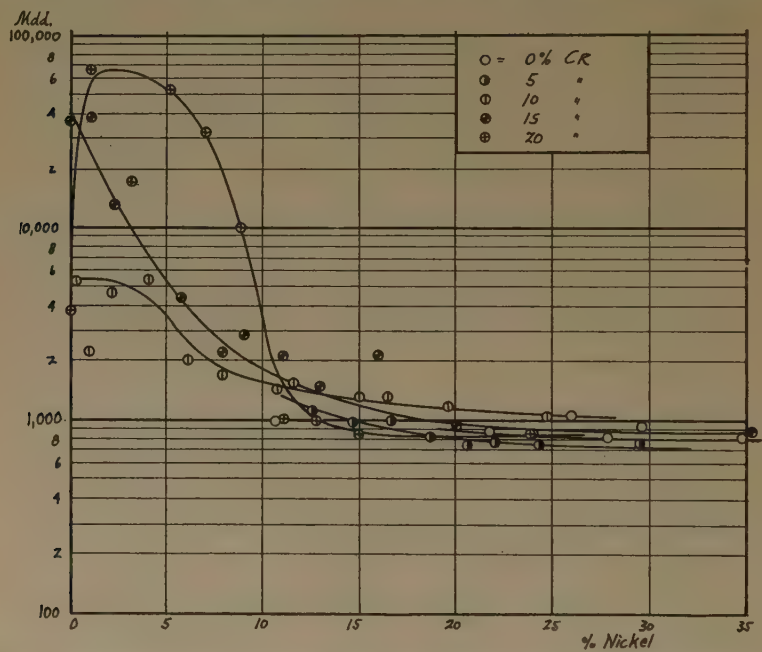

FIG. 7.—CORROSION RATES OF IRON-NICKEL-CHROMIUM ALLOYS IN 5 PER CENT. HYDROCHLORIC ACID.

50,000 Mdd.) is thus reduced by nickel to a fairly constant level (800 to 1200 Mdd.) at the same critical nickel content of 13 per cent., beyond which no important decrease in solubility occurs. Again, this level of corrodibility coincides with that of the nickel steels free from chromium.

Effect of Acid Radical, Concentration, etc., on the Critical Nickel Content.—Is the discontinuous change in solubility at 13 per cent. Ni content independent of the nature and concentration of the corroding acid, or is the observed similarity in action of hydrochloric and sulfuric acids a chance relation? To throw light on this question, which might very naturally be asked, three steels were selected, all containing 15 per cent. Cr and with nickel contents 0, 13 and 20 per cent., respectively. Adher-

ence to the present rule would require that if nickel reduces the solubility in any given acid, the difference in solubility between the 13 and 20 per cent. Ni steels would be small in comparison with the difference between both of them and the nickel-free steel. These steels were then tested following the standard technique (concentrations 5 per cent. by weight, temperature 30° C., time 20 hr.) in 10 different acids other than HCl, H_2SO_4 and HNO_3 and in four different salt solutions[9] of some

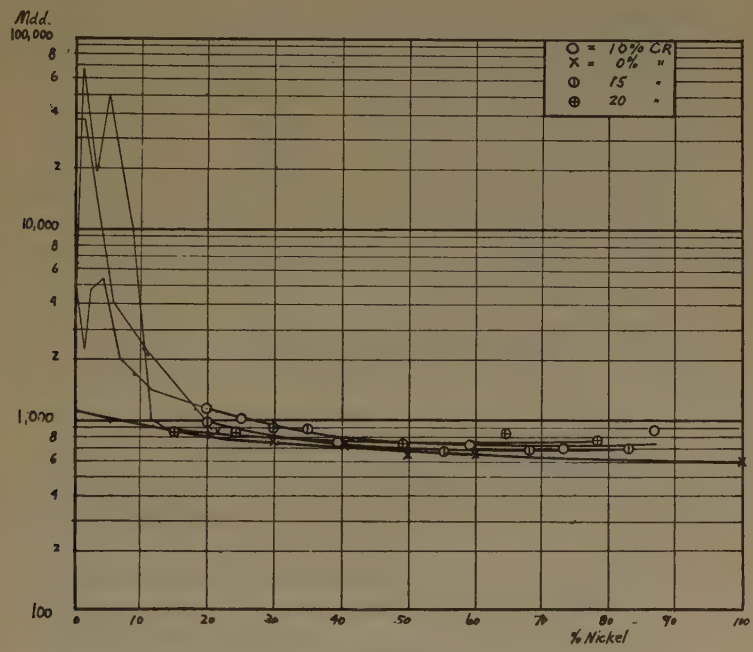

FIG. 8.—CORROSION RATES OF IRON-NICKEL-CHROMIUM ALLOYS IN 5 PER CENT. HYDROCHLORIC ACID.

importance. The results are shown in Fig. 9, from which the following points may be noted:

1. With the exception of sulfurous and phosphoric acids, if nickel reduces the solubility of a chromium steel in a given acid, it does so by depressing the solubility to an approximately constant rate at a nickel content which does not exceed 13 per cent. This holds good for formic, lactic, acetic, tartaric, citric, hydrochloric and sulfuric acids in dilute solution.

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[9] NaCl, 5 per cent.

$CaCl_2$, 20 per cent.

Synthetic sea water [See A. S. Wheeler: Composition of Sea Waters near Beaufort, N. C. *Jnl.* Amer. Chem. Soc. (1910) **32**, 646.]

Synthetic mine water [See *Bull.* No. 4, U. S. Bur. Mines, Coal Mining Investigations, Edna No. 2 Mine].

2. A similar relation holds for such salt solutions as 5 per cent. NaCl, calcium chloride brine and sea water.

3. The solubility of chromium steels in oxalic acid is fairly high and is barely affected by as much as 20 per cent. Ni. The solubility of all three steels in benzoic and carbolic acids and in synthetic mine water is very low.

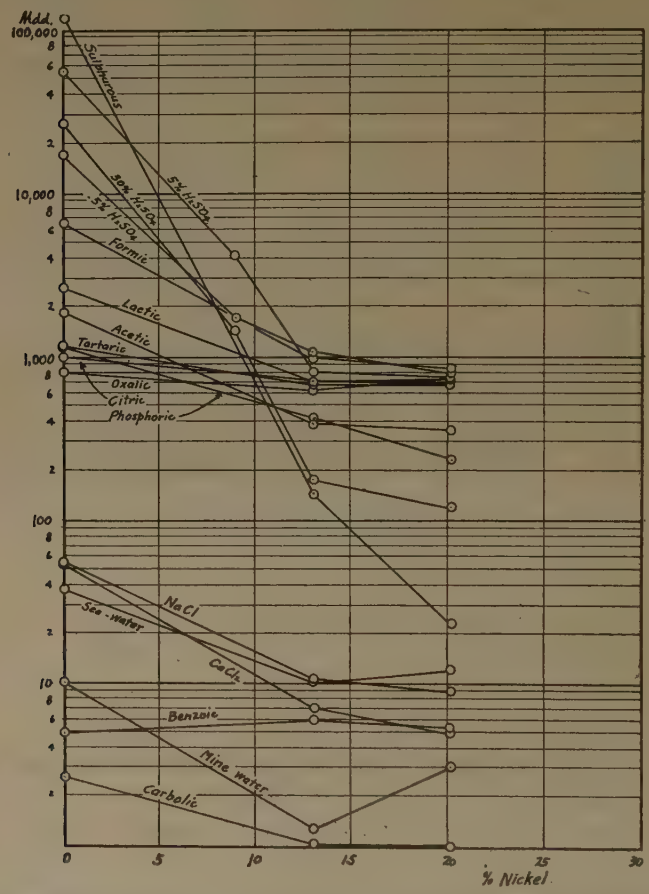

FIG. 9.—EFFECT OF NICKEL ON SOLUBILITY OF NICKEL-CHROMIUM STEELS (15 PER CENT. CR) IN ACIDS, ETC.

There is a definite indication that the discontinuous solubility of nickel-chromium steels is real, and independent of the type of acid within wide limits. Although all of the acids in the strength used are less highly ionized than corresponding weight percentages of hydrochloric or sulfuric acids, a further test was made to be sure that this important nickel concentration does not shift with change in acid concentration.

This was done by adding one more steel (15 per cent. Cr, 9 per cent. Ni) and comparing the solubilities of these in 0.5, 5 and 30 per cent. sulfuric acid. These results are also plotted in Fig. 9 and indicate that within this wide range of hydrogen-ion concentrations the group of steels responds in exactly the same way, the critical nickel content lying in all cases between 9 and 13 per cent. nickel.

Sulfurous Acid and Sulfurous Acid Mixtures

It was shown in the preceding section that sulfurous acid does not behave like the great generality of nonoxidizing acids. Aside from the intrinsic importance of resistance to this substance, it seems certain that sulfurous acid, in the small concentrations in which it occurs in city atmospheres, bears an important relation to the stainlessness of iron-chromium and iron-nickel-chromium alloys when subjected to atmospheric exposure. This will not be given further consideration here, but it is proposed to discuss in some detail various aspects of these alloys in their relation to sulfurous acid.

Sulfur dioxide gas, if anhydrous, is without effect on either iron-nickel, iron-chromium or iron-nickel-chromium alloys. The wet gas, or water solutions containing it, attacks vigorously all iron-nickel alloys and many of the chromium-bearing alloys.

Anticipating somewhat, the measurement of metal solubilities in sulfurous acid solutions has turned out to be rather difficult, owing to a number of special variables peculiar to this acid which are hard to control. These include the volatility of SO_2 in water solutions and the strict necessity of avoiding the formation, by oxidation, of sulfuric acid, both of which require the test to be carried out in closed containers, foregoing agitation and aeration. The reaction descriptive of the corrosion process is very evidently complex and has not been analyzed, making the recognition and control of limiting factors at present impossible. In addition to these obstacles, the interpretation of experimental data is complicated by the fact that in some cases an obstructive insoluble corrosion product forms.

Pure Sulfurous Acid Solutions.—Some preliminary tests were made to find whether the visible stain formed by the action of sulfurous acid is a film capable of retarding corrosion by its presence. Monel metal, a 15 per cent. chromium steel and a nickel-chromium steel were exposed in closed bottles of 5 per cent. H_2SO_3 at 30° C. for varying lengths of time (Fig. 10). It appears that 15 per cent. Cr steel dissolves at a constant velocity expressible as a true rate, while the nickel-copper alloy and the nickel-chromium steel corrode at continuously diminishing velocities. The latter follow curves which on analysis prove to be very nearly parabolic, thus conforming to a behavior in which corrosion is subject to the restraint

of a permeable corrosion product.[10] The difficulty of comparing the solubilities of metals differing fundamentally in law of solution is obvious.

In the weight-loss tests which follow, a double period of exposure was adopted, the second nine times as long as the first, to differentiate the filming from the nonfilming compositions. This can be done readily by inspection, as if no film action occurs the two weight losses would be in the approximate ratio of 1 to 9; if a true film action (parabolic) occurs, this ratio would be 1 to 3.

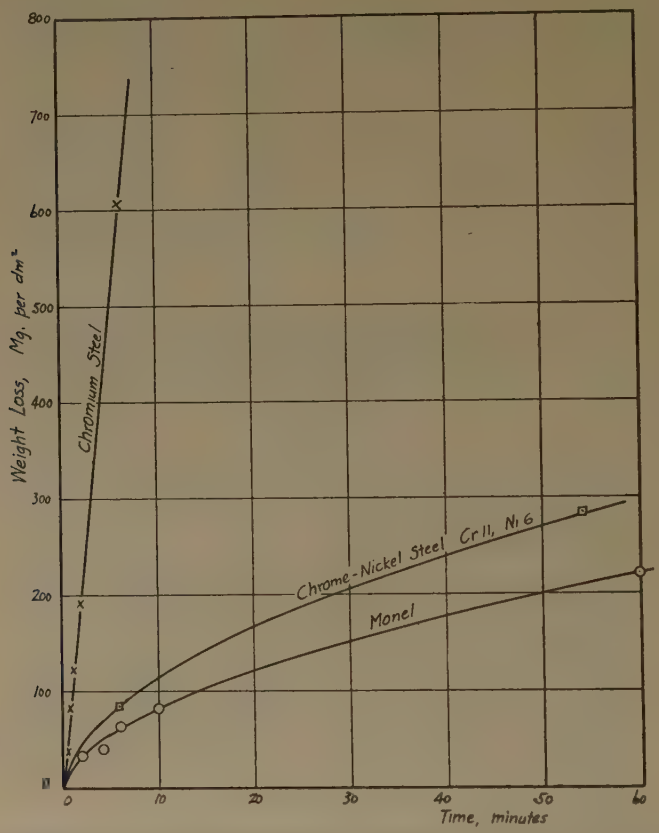

FIG. 10.—RESTRAINED AND UNRESTRAINED CORROSION IN 5 PER CENT. SULFUROUS ACID.

From such a comparison (Table 6) it appears that while the absence of interfering film formation is characteristic of all chromium steels up to 16 per cent. Cr (at which content they cease to be acted on by sulfurous acid) nickel is powerful in bringing about such interference and nearly all the nickel-bearing steels show the filming effect (Fig. 10). The amount of nickel necessary to cause this change is quite small: with

[10] N. B. Pilling and R. E. Bedworth: Oxidation of Metals at High Temperatures. *Jnl.* Inst. Metals (1923) **29.** 529.

4 per cent. Cr, less than 2.5 per cent. Ni; with 10 per cent. Cr, 1.1 to 2.2 per cent. Ni; with 15 per cent. Cr, less than 1.2. per cent. Ni. By virtue of this filming action, small percentages of nickel have a considerable effect on the soluble chromium steels and at 15 per cent. Cr, the addition of 3 per cent. Ni reduces the solubility rate from over 5000 to less than 100 units. This protective action cannot be forecast from the appearance of the corrosion product alone, as heavy, adherent yet wholly unprotective coatings form on the nickel-free steels. A weight

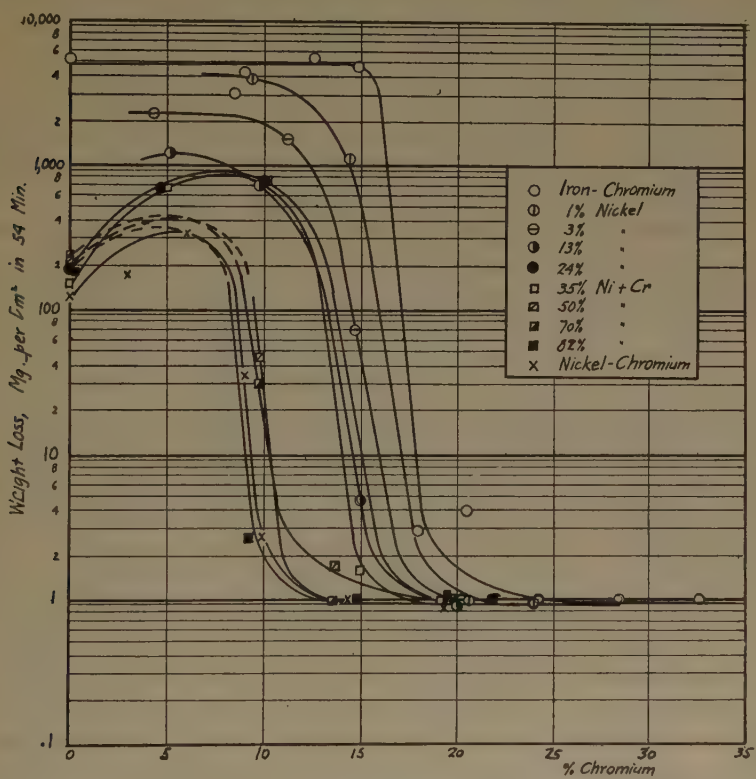

FIG. 11.—CORROSION OF IRON-NCKEL-CHROMIUM ALLOYS IN 5 PER CENT. SULFUROUS ACID.

loss of about 20 mg. per sq. dm. in 54 min. is equivalent to the first appearance of a visible stain.

In a certain superficial sense sulfurous acid resembles strong nitric acid in its action on iron-nickel-chromium alloys. In both cases sharp limits of attack are developed which are almost wholly functions of the chromium content, but here the resemblance ceases. In Fig. 11 a few curves are given showing the sharpness with which the change from high to low solubility occurs at several different proportions of iron and nickel. The trend of the break in the curve to lower chromium concentrations as the nickel content increases may be traced.

The action of chromium in iron-chromium alloys seems simple. Contents of chromium up to 15 per cent. have no effect quantitatively and all steels of lesser chromium content dissolve at a practically uniform, high rate (125,000 Mdd.). Between 15 and 18 per cent. the solubility drops to one-thousandth of its former magnitude.

The information on iron-nickel alloys is less complete; at 20 per cent. Ni the solution rate is only one-tenth that of iron and is almost the same as that of nickel. Between 20 and 100 per cent. Ni, therefore, nickel has scarcely any effect.

In the presence of much nickel, chromium has a peculiar effect in first increasing the rate of solution. This is shown most positively in the range 10 to 30 per cent. Ni where the solution rate is increased threefold or fourfold at 8 to 10 per cent. Cr, beyond which an effective limit of attack is reached. This effect seems to persist down to the nickel-chromium alloys, for which reason three of the curves in Fig. 10 are dotted through a maximum although no alloys of suitable chromium content were available to verify this.

The triaxial plot (Fig. 15) shows the configuration thus developed, with a ridge of maximum solubilities extending parallel to the iron-nickel axis. The first 35 per cent. Ni seems most effective in reducing the chromium content required to induce passivity in sulfurous acid, and the limiting chromium content drops from 16 per cent. Cr with 0 per cent. Ni to 11 per cent. Cr at 35 per cent. Ni and thence to 9 per cent. Cr with 0 per cent. Fe. All chromium contents lying beyond this curve represent alloys unstained and insoluble in pure sulfurous acid solutions.

Effect of Other Electrolytes on the Activity of Sulfurous Acid.—Quite accidentally it was discovered that the presence of small amounts of other substances in sulfurous acid solutions may change their activity against iron-nickel-chromium alloys enormously. A stale solution of H_2SO_3 was noted to stain 15 per cent. Cr, 15 per cent. Ni vigorously, although this steel is normally passive by a good margin. This discrepancy was finally traced to a small content of sulfuric acid in the solution, presumably formed spontaneously by oxidation of sulfurous acid, and many other acids and salts were found to have a similar effect. For example, a steel containing 28 per cent. Cr suffered no detectable corrosion in pure 5 per cent. sulfurous acid; the addition of 5 per cent. NaCl, which itself is also without effect on this steel, brought about a corrosion rate of 95,000 Mdd., as great as that of dilute hydrochloric acid.

A comparison of the stimulating action of a number of such substances on four or five alloys, as shown qualitatively by staining in drop tests, is given in Table 3. A curious irregularity persists throughout and no particular acid or basic ion seems to have a consistent effect. Thus, H_2SO_4 or Na_2SO_4 both accelerate, yet $NiSO_4$ is inert; acetic acid accelerates yet sodium acetate is inert; five acids tried all accelerate,

TABLE 3.—*Effect of Inorganic Compounds on Action of Sulfurous Acid Solutions on Nickel-chromium Steels*

Drop Tests of Six Minutes Duration at Room Temperature

	Additional Compounds in Solution		T893	T1012	T1013	T1002	T1096	
H_2SO_3 Per Cent. by Wt.	Name	Concentration, Grams per Liter	Cr, 14.85 Ni, 0.14	Cr, 15.01 Ni, 13.01	Cr, 14.98 Ni, 20.07	Cr, 21.72 Ni, 24.00	Cr, 20.61 Ni, 11.12	Remarks
5	None		xx	x	x			
	Acetic acid	50	xxxx	xx	xx			No effect if totally immersed.
	Chromous sulfate	50	xx	x	x			
	Cupric sulfate	50	x	x	x			
	Ferric chloride	50		xxx	xxx			
	Ferric sulfate	50		xxx	xxx			
	Ferrous chloride	50	xxxx	xxx	xxx			
	Ferrous sulfate	Saturated	xxxx	xx	xx			
	Hydrochloric acid	50	....	xxx	xxx			
	Hydrogen peroxide c. p.[a]	50	xxxx	xxx	xxx			
	Nickel nitrate	50	xx	x	x			
	Nickel sulfate	50	xx	x	x			
	Nitric acid	50	xxx	xxx	xxx			
	Oxalic acid	50	xxxx	xx	xx			
	Potassium chloride	50	xxxx	xxx	xxx			
	Potassium hydroxide	50	x	x	x			
	Silver nitrate	50	xxxx	xxxx	xxxx			Silver deposited?
	Sodium acetate	50	xx	x	x			
	Sodium borate	50	xx	x	x			
	Sodium bicarbonate	50	x	x	x			
	Sodium carbonate	50	x	x	x			
	Sodium chloride	50	xxxx	xxx	xxx			
	Sodium chloride	5				xxx	xxx	No effect if totally immersed.
	Sodium nitrate	50	xxxx	x	xxx			
	Sodium oxalate	50	xxxx	x	x			
	Sodium silicofluoride	50	xxxx	xx	x			
	Sodium sulfate	50	xxxx	xxx	xxx			
	Sodium sulfide	50	xx	x	x			
	Sulfuric acid	50	....	xxx	xxx			
	Sulfuric acid	1		xxx	xxx			
10	None		xx	x	x			
	Sodium chloride	50	xxxx	xxx	xxx			

[a] 3% solution. x = Bright. xx = Brown stain. xxx = Black ring. xxxx = Black stain.

yet increasing the hydrogen-ion concentration by increasing the sulfurous acid content had no analogous effect.

It is of particular interest to note that two common compounds, sodium chloride and sulfuric acid, both of which may occur with sulfurous acid in industrial atmospheres, are particularly effective, and the action of these two accelerants has been given some attention in detail. In some way the action of sulfurous acid-salt mixtures differs from that of simple sulfurous acid and this is brought out particularly in the drop attack. Pure sulfurous, when it attacks a steel, does so throughout the entire area beneath the drop. When a solution of sodium chloride and

sulfurous acid attacks a steel lying normally beyond the limit of attack in pure sulfurous, the surface beneath the center of the drop remains bright while the margin stains very darkly in a characteristic thin ring. This, of course, suggests the operation of some sort of electrolytic cell.

The few quantitative tests in Table 6 show that the effect of the sodium chloride is not to increase the rate of solution of "soluble" steels but to extend the location of the limit of attack, requiring a higher chromium content to bring about insolubility. A rough estimation of the limit of attack in saline-sulfurous solutions, in comparison with pure sulfurous acid, is given in Fig. 16. The effect is greatest in the chromium steels, where the limit is raised from 16 per cent. Cr to over 33 per cent. Cr. At 15 per cent. Ni the limit rises from 12 to about 23 per cent. Cr, while with the nickel-chromium alloys the change is only from 9 to 13 per cent. Cr. Conceivably these limits are functions of both the nature and the concentration of the auxiliary salt or acid. In the case of 5 per cent. NaCl, 5 per cent. H_2SO_3 the limit of attack is even higher with a drop exposure in the open air than with full immersion in the nonaerated solution, rising at 15 per cent. Ni to more than 30 per cent. Cr. No simple, malleable iron-nickel-chromium alloy of any proportions yet available has offered substantial resistance to this kind of attack involving the simultaneous presence of sodium chloride, oxygen and sulfurous acid. Long exposures of a wide variety of alloys of this group in natural atmospheres have shown that none of these, containing even more than 20 per cent. chromium content, is truly stainless.

The amount of accelerating substance needed to provoke staining on an alloy otherwise proof against sulfurous acid is not great. It is truly surprising to find, with an alloy containing 15 per cent. Cr, 15 per cent. Ni, that 0.08 per cent. sulfuric acid or 0.8 per cent. sodium chloride in 5 per cent. sulfurous acid, or 0.02 per cent. sulfurous acid in 5 per cent. sodium chloride suffice to change the behavior of these solutions from complete inertness to great activity.

Effect of Constitution and Heat Treatment

It seems to be generally true, as study of these solubility tests will show, that lattice structure has no important effect on corrosion rates. In sulfuric and hydrochloric acids, the curves traverse the martensitic field from ferritic to austenitic alloys in a smooth curve with no breaks corresponding to the phase changes, and both ferritic and austenitic alloys may release gaseous hydrogen from these acids. In nitric acid purely α lattice alloys and purely γ lattice alloys may show quantitatively identical relations between chromium content and solubility, and in sulfurous acid the limit of attack cuts across the ternary diagram with great indifference to structural conditions. It is, apparently, concentration of particular elements in solid solution which counts.

TABLE 4.—*Effect of Heat Treatment of Chromium Steel on Acid Solubility* (35° C.)

Cr, 11.80 Per Cent.; Ni, Nil.; C, 0.10 Per Cent.

Heat Treatment	5 Per Cent. H_2SO_4 Mdd.	5 Per Cent. HNO_3 Mdd.	5 Per Cent. H_2SO_3[a]
Hot-rolled	7,000	10,500	
950° C., ½ hr. OQ	8,430	3,800	4,980
950° C., ½ hr. OQ + 300° C., 1 hr. WQ	8,890	4,200	
950° C., ½ hr. OQ + 400° C., 1 hr. WQ	8,370	4,300	
950° C., ½ hr. OQ + 500° C., 1 hr. WQ	7,300	13,200	
950° C., ½ hr. OQ + 600° C., 1 hr. WQ	6,730	13,200	
950° C., ½ hr. OQ + 700° C., 1 hr. WQ	7,090	9,400	4,760
950° C., ½ hr. OQ + 800° C., 1 hr. WQ	8,550	6,400	
850° C., ½ hr. OQ + 500° C., 1 hr. WQ	7,640	27,900	
1,050° C., ½ hr. OQ + 500° C., 1 hr. WQ	6,330	14,000	
850° C., ½ hr. OQ + 700° C., 1 hr. WQ	6,670	10,300	
1,050° C., ½ hr. OQ + 700° C., 1 hr. WQ	6,110	10,400	
1,250° C., ½ hr. OQ + 700° C., 1 hr. WQ	5,080	8,800	
950° C., ½ hr. furnace cool	4,800	13,000	
1,200° C., ¼ hr. furnace cool	31,100	4,800	

[a] 54 min. weight loss (Mg. per sq. dm.).

TABLE 5.—*Effect of Heat Treatment of Nickel-chromium Steels on Solubility (Mdd.) in 5 Per Cent. H_2SO_4* (35° C.)

Heat Treatment		S 278	O 331	O 283
	Ni	15.46	10.33	8.06
	Cr	15.04	15.57	17.65
	C	0.23	0.12	0.14
Hot-rolled		906		9,230
600° C., 1 hr., WQ		799		10,830
800° C., ½ hr., WQ		804		6,000
1,000° C., ½ hr., WQ		812		1,035
1,200° C., ¼ hr., WQ		735	958	858
600° C., 1 hr., AC		785	3,070	19,900
800° C., ½ hr., AC		758	1,180	13,550
1,000° C., ½ hr., AC		750	943	2,410
1,200° C., ¼ hr., AC		842		1,155
1,000° C. + 700° C., 2 hr., WQ		794	1,022	7,950
1,000° C. + 700° C., 24 hr., WQ		770	1,640	4,720
950° C., ½ hr., FC		753	4,510	5,860
1,200° C., ¼ hr., FC			1,745	2,040

The effect of heat treatment on the acid solubility of a few typical alloys (hot-rolled from rather large melts) is shown in Tables 4 and 5. It is not surprising to find that it is principally the phase changes that result in changes in concentration of chromium in solid solution that affect these solubilities.

TABLE 6.—*Solubility Tests (Standard Testing Technique)*

Melt Number	Analysis			5 Per Cent. H_2SO_4		5 Per Cent. HCl		5 Per Cent. HNO_3		35 Per Cent. HNO_3		5 Per Cent. H_2SO_3		5 Per Cent. H_2SO_3 + 5 Per Cent. NaCl	
				Duration	Corrosion Rate	Duration	Corrosion Rate	Duration	Corrosion Rate	Duration	Corrosion Rate	Weight Loss Mg. per Sq. Dm.		Weight Loss Mg. per Sq. Dm.	
	Cr	Ni	C	Hr.	Mdd.	Hr.	Mdd.	Hr.	Mdd.	Hr.	Mdd.	6 Min.	54 Min.	6 Min.	54 Min.
								Chromium = 0							
T-347[a b]			0.04	20	1,160	20	1,076	1	469,000						
1674		5.29	0.03	20	817										
1675		10.55	0.02	20	950										
1676		13.35	0.02	20	819										
1677		20.21	0.02	20	663	20	817	1	442,000	2.5	355,000	96	148		
369[a]		19.95	0.07	20	1,030	20	883	1	417,000	2.5	357,000	88	186		
1058		21.83	0.02	20	908	20	846	1	423,000	2.5	357,000	88	155		
1059		24.05	0.02	20	1,000	20	1,047	1	415,000	2.5	365,000	109	148		
1060		26.01	0.02	20	777	20	820	1	371,000	2.42	1,145,000	109	151		
1062		27.93	0.02	20	778	20	927	1	303,000						
1063		29.74	0.05	20	776	20	825	1	291,000	2.5	520,000	116	152		
304[a]		28.44	0.11	20	655	20	814	1	283,000						
1064		34.90	0.01	20	818	20	732	1	192,000			122	217		
361[a]		39.89	0.07	20	675	20	628	1	57,800			(289)[d]	(839)		
360[a]		49.48	0.02	20	610	20	639	1	32,300			107	226		
370[a]		59.55	0.05	20	658	20						85	182		
359[a]		59.61	0.04									79	132		
1349		68.48	0.03									87	129		
1350		77.86	0.03				610[e]	1	5,000						
1351		88.65	0.04	20	580	20									
0203[a]		99.+													
								Chromium = 5 per cent.							
1037	5.09	12.66	0.03	20	1,009	20	1,108	1	224,000	.83	40	590	1,255		
1038	4.91	14.75	0.02	20	988	20	1,004	1	227,000	.83	10,500	498	1,012		
1039	4.85	16.63	0.02	20	870	20	1,005	1	232,000	.83	2,250	454	856		
1052	4.98	18.66	0.05	20	710	20	810	1	190,000	.83	6,800	394	951		
1053	5.05	20.65	0.04	20	670	20	730	1	169,000	.83	32,700	384	886		
1054	4.98	22.22	0.08	20	720	20	760	1	189,000	.83	39	362	843		
1055	4.80	24.41	0.07	20	719	20	740	1	249,000	.83	42	343	687		
1056	5.02	29.70	0.05	20	653	20	754	1	170,000	.83	26	301	686		

							Chromium = 10 per cent.								
833	9.00	.21	0.22	20	21,900	20	5,280	1	110,000	20	13	598	4,270		
834	9.32	1.11	0.14	20	15,600	20	2,390	1	57,600	20	85	624	3,890		
839	11.23	2.22	0.11	20	15,600	20	4,860	1	10,800	20	8	605	(18)		
835	10.33	4.22	0.22	20	6,600	20	5,450	1	73,300	20	11	396	1,990		
838	11.20	6.06	0.27	20	2,600	20	1,960	1	68,100	20	11	85	290		
844	11.49	8.04	0.13	20	1,740	20	1,750	1	5,910	20	7	(5)	(1)		
845	8.89	10.56	0.12	20	1,310	20	1,280	1	22,100	20	10	269	2,300		
1014	10.02	10.61	0.05	20	1,470	20	1,380	1	21,900	20	5	39	(93)		
1015	9.77	12.85	0.09	20	810	20	1,590	1	22,400	20	6	15	700		
1016	9.76	14.99	0.10	20	890	20	1,300	1	44,000	20	11	2	700		
1003	11.73	15.96	0.14	20	740	20	2,190	1	34,200	20	7	7	(21)		
1017	9.83	16.47	0.11	20	730	20	1,340	1	48,500	20	6	9	725		
1018	9.88	19.73	0.06	20	700	20	1,200	1	42,100	20	7	6	670		
1057	9.96	24.81	0.11	20	690	20	1,020	1	44,800	20	6	6	770		
1131[f]	9.73	39.21	0.06	20	720	20	730	1	14,300	20	11	2	46		
1139[f]	9.70	58.53	0.07	20	760	20	720	1	16,700	20	10	6	30		
1143[f]	9.08	72.97	0.04	20	570	20	700	1	7,650	20	10	nil	3		
1147[f]	9.80	87.37	0.02	20	740	20	890	1	3,450	20	12	2	3	3	143
							Chromium = 12 per cent.								
1026	12.60		0.11	20	27,000	20	9,960	1	9,140	20	19	649	5,400		
				7	24,800	3	3,510								
420[a]	12.18	10.43	0.28	20	1,550	20	1,600	1	35,800	20	10	143	592		
							Chromium = 15 per cent.								
893	14.85	0.14	0.25	20	54,900	20	37,100	1	7,150	20	11	680	4,550	650	4,320
				3	28,100	3	10,600								
894	14.36	1.19	0.21	20	42,100	20	39,100	1	10,600	20	8	607	1,053		
896	14.62	3.34	0.21	20	15,700	20	13,000	1	4,400	20	9	92	4		
898	14.34	5.93	0.23	20	5,640	20	4,340	1	10,700	20	10	2	3		
899	14.61	7.87	0.17	20	4,460	20	2,380	1	10,100	20	12	4	(39)		
1010	15.21	9.01	0.07	20	4,020	20	2,970	1	6,310	20	3	1	9		
842	14.31	10.70	0.21	20	770	20	1,000	1	5,520	20	3	nil	1		
1011	15.09	11.07	0.18	20	1,960	20	2,090	1	16,700	20	5	nil	nil		
1012	15.01	13.01	0.12	20	790	20	1,470	1	11,200	20	5	1	5	8	236
1013	14.98	20.07	0.07	20	750	20	950	1	6,650	20	5	+0.5[g]	2	3	373
1132[f]	13.63	35.34	0.07	20	690	20	880	1	2,490	20	5	+0.5	2	4	554
1140[f]	13.56	54.61	0.04	20	770	20	670	1	5,880	20	2	0.5	nil		
1168[f]	14.75	68.10	0.05	20	640	20	690	1	8,230	20	5	nil	1.0		
1148[f]	14.31	82.86	0.04	20	780	20	700	1	3,620	20	11	4	nil	1	4

TABLE 6.—(*Continued*)

Melt Number	Analysis			5 Per Cent. H_2SO_4		5 Per Cent. HCl		5 Per Cent. HNO_3		35 Per Cent. HNO_3		5 Per Cent. H_2SO_3		5 Per Cent. H_2SO_3 + 5 Per Cent. NaCl	
				Duration	Corrosion Rate	Duration	Corrosion Rate	Duration	Corrosion Rate	Duration	Corrosion Rate	Weight Loss Mg per Sq. Dm.		Weight Loss Mg per Sq. Dm.	
	Cr	Ni	C	Hr.	Mdd.	Hr.	Mdd.	Hr.	Mdd.	Hr.	Mdd.	6 Min.	54 Min.	6 Min.	54 Min.
							Chromium = 20 per cent.								
1075	20.46	0.11	0.18	3	19,300	3	3,850	1	340	20	17	557	4	552	3,498
						20	3,800								
1005	20.60	1.14	0.09	20	80,500	20	61,700	1	480	20	4	3	nil		
1006	20.54	3.10	0.08	20	28,900	20	18,100	1	740	20	3	3	+0.5		
1007	20.49	5.08	0.11	20	32,900	20	53,800	1	640	20	6	4	2		
1008	20.41	7.00	0.08	20	26,100	20	31,800	1	880	20	4	2	6		
1009	20.31	8.87	0.10	20	13,400	20	10,100	1	960	20	4	(10)	(9)	5	180
1096	20.61	11.12	0.09	20	1,450	20	1,030	1	4,670	20	4	1	nil		
1095	20.00	12.78	0.09	20	1,020	20	1,030	1	4,340	20	4	2	+0.8		
1065	19.19	15.00	0.15	20	790	20	850	1	2,380	20	6	3	nil	3	177
1002	21.72	24.00	0.38	20	710	20	850	1	410	20	3	5	0.6	1	2
657	22.07	21.95	0.14	20	840	20	870	1	3,290			nil	nil		
1133′	19.48	29.80	0.07	20	800	20	750	1	500	20	nil	nil	nil		
1142′	18.75	29.90	0.15	20	890	20	900	1	1,280	20	50	(17)	(3)		
1141′	19.79	48.82	0.06	20	790	20	720	1	280	20	2	0.8	+0.8	nil	nil
1145′	19.09	63.61	0.06	20	700	20	830	1	280	20	7	+0.9	nil		
1149′	18.84	78.29	0.07	20	900	20	760	1	740	20	24	nil	0.9	nil	nil
							Chromium = 24 per cent.								
1097	24.20	0.13	0.13	20	91,300	3	20,800	1	343	20	1	4	0.6		
				3	51,200										
1076	24.10	1.20	0.21	3	31,500	1	14,100	1	161	20	9	nil	0.6		
						2	7,700								
						3	15,300								
						7	48,000								
						20	61,600								
						41	57,600								

							Chromium = 29 per cent.								
1098	28.30	0.16	0.19	20	94,600	3	43,600	1	190	20	nil	3	+0.7	510	3,640
				7	126,000										
				3	67,000										
1077	28.78	0.43	0.26	3	75,800	3	32,500	1	113	20	15	2	nil		
1320	28.98	15.18	0.23	20	7,980[h]									nil[e]	nil
							Varying Chromium, Nickel = 0								
347[a b]			0.04	20	1,160	20	1,076	1	469,000						
1074	8.39	0.05	0.11	20	9,640	20	1,730	1	94,200	20	1,340	410	3,040		
						3	1,740								
1026	12.60		0.11	20	27,000	20	9,960	1	9,140	20	19	649	5,400		
				7	24,800	3	3,510								
893	14.85	0.14	0.25	20	54,900	20	37,100	1	7,150	20	11	680	4,550	650	4,320
				3	28,100	3	10,600								
1004	18.03	0.20	0.13	20	41,000	20	17,600	1	550	20	4	2	3		
						3	4,700								
1075	20.46	0.11	0.18	3	19,300	3	3,850	1	340	20	17	557	4	552	3,498
						20	3,800								
1097	24.20	0.13	0.12	20	91,300	3	20,800	1	343	20	1	4	0.6		
				3	51,200										
1098	28.30	0.16	0.19	20	94,600	3	43,600	1	190	20	nil	3	+0.7	509	3,640
				7	126,000										
				3	67,000										
1078	32.55	0.18	0.18	3	118,000	3	107,000	1	88	20	17	0.6	0.7	436	1,514
						1	26,200								
							Iron = 0								
1359	2.85	93.00	0.08									8	178		
1360	5.76	92.40	0.03									10	396		
1361	8.55	89.22	0.08									116	34		
							Miscellaneous								
469[a]	1.99	5.03	0.07									655	3,300		
471[a]	6.03	0.33	0.16									766	5,350		
472[a]	4.25	2.48	0.20									875	2,145		
473[a]	8.29	0.39	0.38									643	4,510		

NOTES.—[a] = Specimen 1 by 1 by 0.05 in., cut from annealed cold-rolled sheet.
[b] = Remelted Armco iron.
[c] = Average of two tests.
[d] = Data inclosed by parentheses are thought not to be indications of general trend.
[e] = Solution contained 2 g. per liter. H_2SO_4 in 5 per cent. H_2SO_3; no NaCl.
[f] = Standard disk specimens cut from annealed ¾-in. dia. cast bar.
[g] = + indicates a *gain* in weight.
[h] = Tested at 35° C.

The annealing of hardened high-chromium steel withdraws chromium from solution by the precipitation of iron-chromium carbides, and the fact that hardening (oil quench) a 12 per cent. Cr steel decreases its solubility in dilute nitric acid, increases it in dilute sulfuric acid and is without effect in sulfurous acid, in comparison with the annealed or tempered steel, is wholly in agreement with the dependence of solubility rate on chromium content developed experimentally.

It would seem that, theoretically, heat treatment should have but slight effect in the solubility of the low-carbon austenitic iron-nickel-chromium alloys, yet this is true only for those alloys containing more than the critical content of nickel. The alloys containing chromium and from 5 to 13 per cent. Ni exhibit greatly diminished solubilities in dilute sulfuric acid when they have been cooled rather rapidly from temperatures above 1000° C., and the magnitude of the change seems to preclude its connection with the solution of carbides.

The examples show that the high solubilities characteristic of this particular group in the well-annealed condition may be reduced to the level of the high-nickel alloys and the shift in critical nickel content thus indicated is to below 8 per cent. Ni at the least. It is not known that this heat treatment brings about any structural or lattice change not shared by the alloys of higher nickel content.

General Discussion

The dependence of corrosion rate on complete composition is shown in the three-coordinate plots, Figs. 12 to 16. It would seem that the principal points established are:

1. Discontinuous changes in solubility, or limits of attack, occur in the corrosion of iron-nickel-chromium alloys.

2. In hydrogen-discharging acids the limit of attack is a function of the nickel content only and takes the form of an abrupt termination to a more or less steady diminution in corrosion rate. This nickel content is about 13 per cent., and alloys having higher nickel contents corrode in fully aerated, agitated solutions at a constant rate which is independent of the nickel or chromium or iron contents. While this rate depends, in magnitude, on the H-ion concentration as well as the nature of the acid radical, the critical nickel content does not. The latter bears no relation to either the microstructure or the lattice structure of the alloys, yet a particular heat treatment, apparently without effect on either of these, has a profound effect on the location of the limit of attack.

3. The solubility in nitric acid of sufficient dilution to afford rapid rates of corrosion may be affected by changes in content of nickel, chromium or iron, yet the points at which substantial passivity is reached depend practically wholly on the chromium content, independent of

nickel or iron. The chromium content necessary to induce passivity is a continuously changing function of the nitric acid concentration.

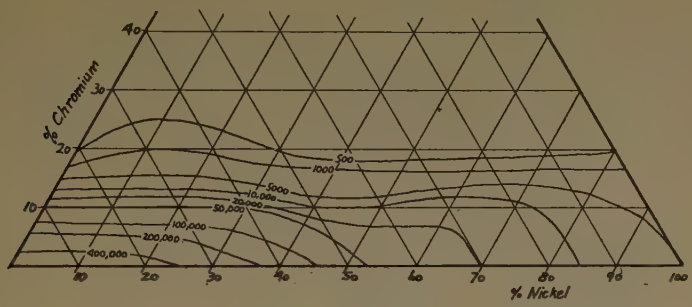

FIG. 12.—EFFECT OF 5 PER CENT. NITRIC ACID.

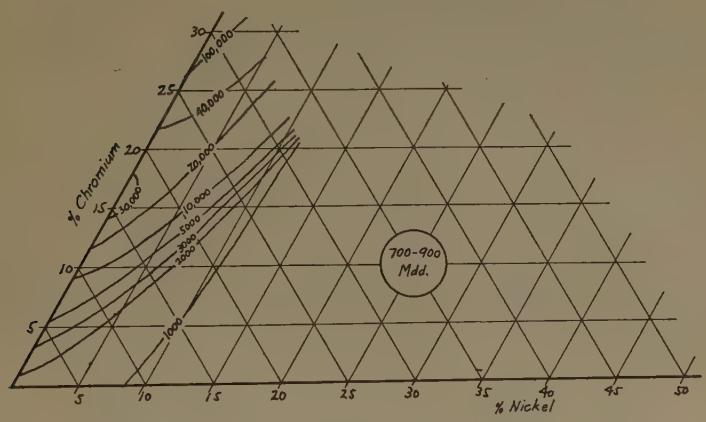

FIG. 13.—EFFECT OF 5 PER CENT. SULFURIC ACID.

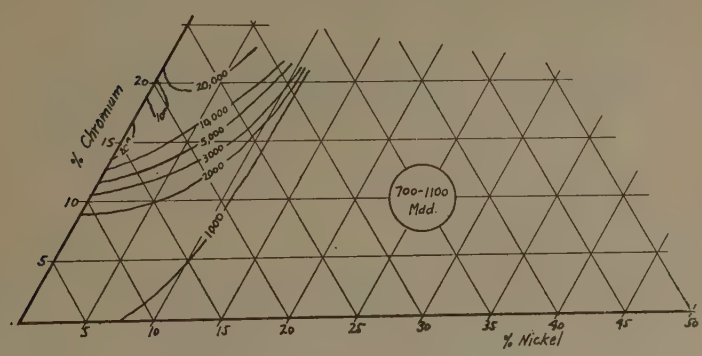

FIG. 14.—EFFECT OF 5 PER CENT. HYDROCHLORIC ACID.

4. The behavior of these alloys in sulfurous acid is highly dependent on the presence of other soluble substances in the acid. In the pure aqueous acid there occur very sharp drops in solubility to complete inert-

ness, and while these are most closely related to the chromium content, the limit is reached at progressively lower chromium contents as the nickel content is increased. The presence of many other salts and acids in sulfurous acid, even in minute amounts, makes a greatly increased chromium content necessary for the display of passivity to the solution.

5. In approximately homogeneous solid solutions of these elements, no relation has been found between microstructure or lattice structure

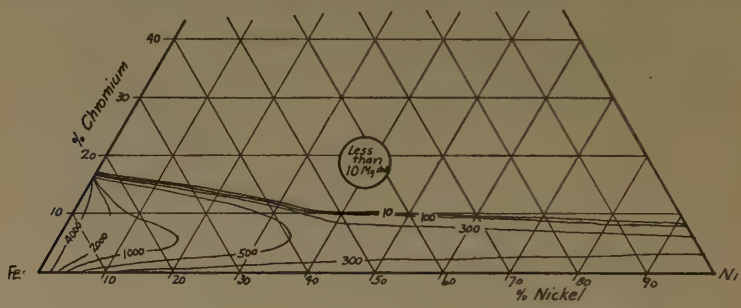

FIG. 15.—CORROSION RATES IN 5 PER CENT. SULFUROUS ACID.

and any limit of attack. The latter are indifferent to the distinctions between the various ferritic aggregations, martensite or austenite.

These results are not in complete harmony with some of the principal investigations which have previously covered portions of this ground. To a considerable extent it is believed that the failure to recognize the function and importance of aeration in corrosion behavior as well as the

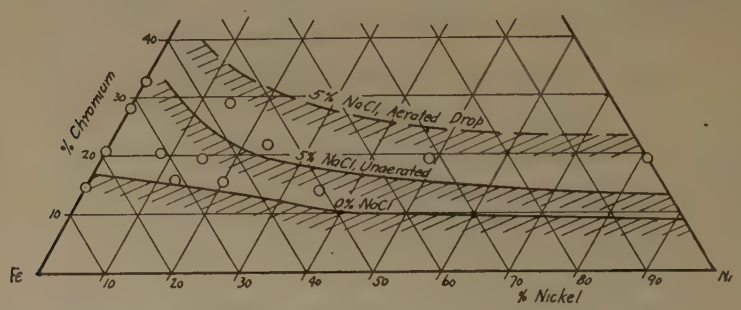

FIG. 16.—EFFECT OF NaCl ON LIMITS OF ATTACK IN 5 PER CENT. SULFUROUS ACID.

lack of some other elements of control are accountable for this difference. For example, we differ with Hatfield,[11] who believes that the addition of nickel to chromium steels increases their resistance to nitric acid, and with Utida and Saito[12] who conclude that high chromium contents of

[11] W. H. Hatfield: Influence of Nickel and Chromium upon the Solubility of Steel (in Relation to Corrosion). *Jnl.* Iron and Steel Inst. (1923) **108,** 103.

[12] Y. Utida and M. Saito: Influence of Metallic Elements on the Corrosion of Iron and Steel. *Sci. Repts.* Tohoku Imp. Univ. [1] (1925) **14,** 295.

the order of 30 per cent., without nickel, result in very low solubility in dilute sulfuric acid and that the addition of chromium increases the resistance of nickel steels to both hydrochloric and sulfuric acids. All of these investigators observed a continuous decrease in solubility in the last-named acids with rising nickel, even to high contents, and failed to find the reduction to constant solubility of the present report. In a recently published article[13] which appeared as this was written, Guertler and Ackermann found such a relation in dilute sulfuric but not in hydrochloric acid.

About 10 years ago Tammann[14] developed his theory of metallic corrosion embodied in the famous theory of molar eighths, which states that a solid solution of two cubically crystalline metals, one of which is attacked by a given solution and the other is not, becomes suddenly inert to that solution when the concentration of the nobler metal reaches ⅛ atomic per cent. or some whole-number multiple of it. This effort to connect the corrosion resistance of alloys to a property of the crystalline lattice was boldly conceived and had an apparent verification in several important examples. It has enjoyed much popularity in Germany and has received further application at the hands of more recent investigators,[15] both of whom profess to have found a rigid adherence to this rule in the case of iron-chromium alloys in nitric acid solutions at ⅛ mole Cr (11.7 per cent. Cr by weight). The latter have also examined a portion of the iron-nickel-chromium series, reporting a similar relation with nitric acid, and also find a sharp drop in sulfuric acid solubility at ⅛ mole nickel (13.1 per cent. Ni by weight), in close agreement, of course, with the present result. Perhaps the most careful and critical test given to Tammann's rule is that by Van Liempt[16] with tungsten-molybdenum alloys, who was compelled to conclude that the concentration of the nobler element at the limit of attack not only departed widely from the required ⅛ portion, but was variable and highly dependent on particulars of the test environment. Besides this direct refutation, it may well be objected that such preoccupation with crystallographic factors ignores the apparently well-established demonstrations of the

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[13] W. Guertler and W. Ackermann: Some Investigations on the Acid Resistance of Chromium-nickel-iron Alloys of High Purity. *Ztsch. f. Metallkunde* (1928) **20,** 269.

[14] G. Tammann: The Chemical and Galvanic Properties of Mixed Crystal Systems and Their Atomic Arrangement. *Ztsch. f. anorg. Chem.* (1919) **107,** 1.

[15] G. Grube and W. V. Fleischbein: Surface Improvement of Metals by Diffusion. I. Diffusion of Chromium into Iron and the Limits of Resistance of Mixed Crystals of Chromium and Iron. *Ztsch. anorg. Chem.* (1926) **154,** 314.

W. Guertler and W. Ackermann: Some Investigations on the Acid Resistance of Chromium-nickel-iron Alloys of High Purity. *Ztsch. f. Metallkunde* (1928) **20,** 269.

[16] J. A. M. Van Liempt: Notes on Resistance Limits of Tungsten-molybdenum Mixed Crystals. *Rec. des Travaux de Pay-Bas* (1926) **45,** 508. See also N. B. Pilling: Tammann's Rule and Corrosion-resistant Alloys. *Min. & Met.* (1927) **8,** 319.

electrochemical nature of corrosion as recently elaborated by Evans, McKay and others.[17]

Despite the apparent conformity to Tammann's rule shown by the existence of a limit of attack at 13 per cent. Ni in hydrogen-discharging acids, we believe that our results offer other and more convincing evidence that space-lattice considerations within the metal are not determinative of corrosion resistance. The following might be mentioned:

1. The critical nickel content, although constant for a wide range of conditions, does shift with a particular heat treatment not known to be connected with any phase or lattice change.

2. The limit of attack (Cr) in pure sulfurous acid changes with change in nickel content and the progress from alloys having the α lattice to those with the γ lattice is effected with no discontinuity. The limits are so sharp that the failure to conform to $\frac{1}{8}$ mole Cr is unmistakable.

3. The limit of attack of chromium steels in nitric acid does not occur at a fixed chromium content but varies through a wide range continuously with the acid concentration.

These and other facts, including the constant rate of corrosion of high nickel-content alloys independent of their composition, seem to be understandable from considerations of electrolytic cell action, polarization, film formation, and other factors related to the environment of the corroding surface. This interesting subject, however, is beyond the intended scope of this paper.

Acknowledgment

The authors wish to express their sense of indebtedness to many of their associates for helpful advice, and to acknowledge gratefully the aid and encouragement freely given them by Paul D. Merica and A. J. Wadhams.

DISCUSSION

U. R. Evans, Cambridge, England.—Is the nature of the attack fairly uniform, or is it localized? So often, localized corrosion occurs under conditions roughly on the boundary between the passive region and the active region. Sometimes in corrosion by neutral or slightly alkaline liquids, fairly general corrosion occurs when conditions are such as to favor the active state, but it becomes localized on approaching the conditions at which passivity sets in.

Dr. Hedges, of London, has found that when one is passing from the active to the passive region, there is often an intervening region in which periodic fluctuations between the active and passive states are observed.

I believe that neither of these phenomena are so common in acid solutions as in approximately neutral solutions, but it would be interesting to me, and possibly to others, to know whether anything of the sort has been met with.

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[17] U. R. Evans: *Op. cit.*

N. B. Pilling.—We have found corrosion under the conditions of our tests usually to be quite uniform except when hydrogen gas is discharged; in this case the surface may become roughened. When the corrosion is such that no visible gas in bubble form is produced and depolarization occurs by oxidation, the corroded surface remains smooth. Even at concentrations of nitric acid which bring about border-line passivity, the attack appears uniform. We have had several interesting experiences with periodicity and perhaps Mr. Ackerman will describe them for you.

D. E. Ackerman.—Periodicity of solution was observed with some nickel-iron alloys in some nitric acid solutions but not with iron-nickel-chromium alloys. The phenomenon is very striking. During the active phase the metal surface is covered with a brown film which is apparently made up of oxides of nitrogen. After a time this gas film appears to be swept off, and a less active or perhaps a passive condition is established. During the existence of this second condition the specimen surface is silvery white; the change from the more active to the less active condition starts at the lowest point of the specimen and rapidly spreads upward over the whole specimen surface, giving the effect of sweeping off the gas film which is characteristic of the more active state. The dislodged gas can be seen to rise through the solution in bubbles which burst upon reaching the surface, releasing a heavy brown gas. The subsequent reversion to the active condition takes place practically simultaneously over the whole specimen surface, as judged by the appearance of the gas film.

These remarks are based entirely upon a few observations made incidentally in the course of our investigation; these observations indicate that the appearance of the phenomenon of periodicity of solution is dependent, among other factors, upon the alloy composition and the nitric acid concentration. A formal study of the phenomenon, such as would disclose all of the important conditions controlling it, would have been outside the scope of the present investigation.

Corrosion of Metals in the Lehigh Valley*

By C. E. Reinhard,† Palmerton, Pa.

(New York Meeting, February, 1929)

A useful accelerated weathering test should be capable of placing any series of metals quantitatively in the same order of endurance as that noted under a particular set of actual exposure conditions. The development of such a test must necessarily depend to a considerable extent upon data obtained from a wide variety of exposures.

This paper offers preliminary data from exposure tests on nine metals placed in 11 locations in the Lehigh Valley, within a radius of 20 miles from Palmerton. The exposure conditions vary from a severe industrial atmosphere to a pure rural atmosphere. The data are offered as evidence of the necessity for the identification and evaluation of the variables of corrosion and as illustration of some of the variations to be considered in the development of a useful accelerated test.

It is quite clear, from this evidence, that a useful accelerated test must be versatile to the extent of showing the probable variations of corrosion resulting from differences in atmosphere as well as from differences in the metals.

The paper is presented solely with the object of pointing out the wide variations in relative merits of several common metals in resisting corrosion and without any thought of initiating controversy regarding the merits of particular metals. For this reason the metals are designated only by symbols in the tables and no key is given to these symbols.

Test Procedure

Specimens, 4 by 6 in., were cut to accurate dimensions from each of the following metals or alloys: aluminum, ascoloy, copper, copper steel, galvanized iron, and zinc. Additional grades of these metals bring the total to nine types. Since it was impossible to obtain the required number of copper-steel specimens having equal surface conditions of rust and scale, it was thought advisable to pickle these specimens in a hot solution of 10 per cent. sulfuric acid. All other specimens were carefully cleaned in ether and alcohol and weighed just prior to exposure.

Four specimens of each type of metal were mounted on a test rack by means of porcelain insulators. The racks were so constructed that

* Contribution from the Research Division, New Jersey Zinc Co.

† Investigator, Metal Section, Research Division, New Jersey Zinc Co.

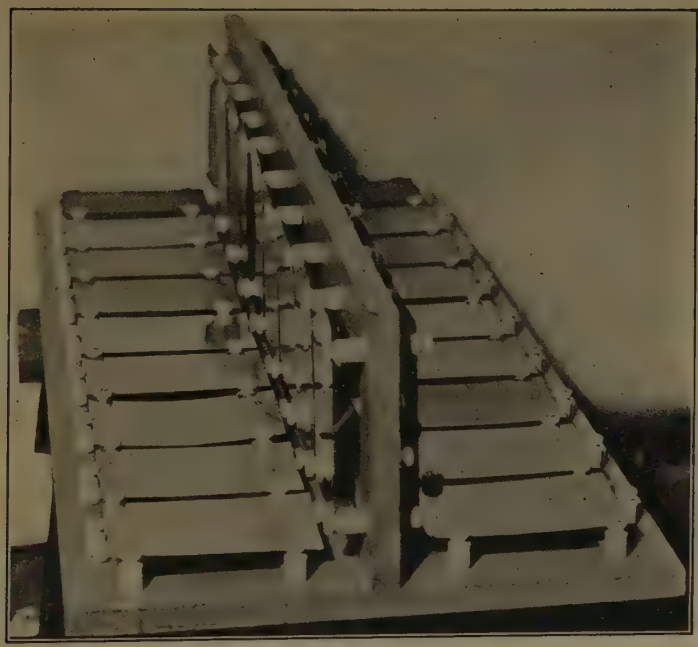

FIG. 1.—SPECIMENS MOUNTED ON TEST RACKS.

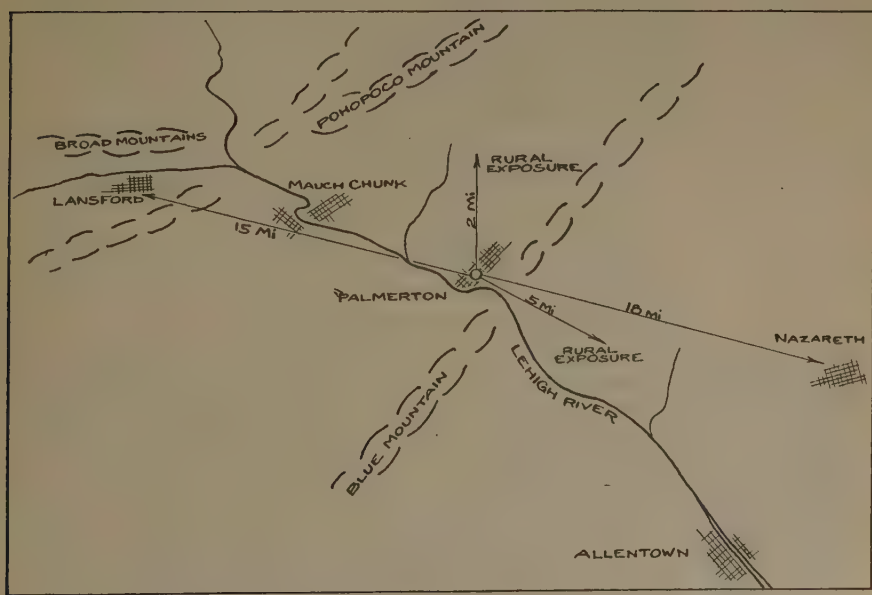

FIG. 2.—LEHIGH VALLEY REGION, SHOWING LOCATION OF TEST RACKS.

single specimens were exposed in both the horizontal and the vertical positions on each side of the rack (Fig. 1). This arrangement permitted the exposure of a single specimen of each base metal in each position in two compass directions. All racks were exposed so that one side faced the east and the other the west.

Two identical racks were placed at each location; one to be inspected periodically, the other to remain exposed for an indefinite time before inspection.

Various types of atmospheres in the Lehigh Valley within a radius about 20 miles from Palmerton were chosen, as follows; (1) coal region; (2) cement district; (3) zinc-oxide furnace building; (4) rural; (5) Palmerton.

A key is given herewith to the rack number and location of the test racks, shown diagrammatically in Fig. 2. Throughout this paper the rack number only will be referred to, since the purpose of the paper is to call attention to the range of variation with a small radius of testing rather than to emphasize the effects at any particular location.

Key to Rack Number and Location of Test Racks

Rack Number	Location
1	New Jersey Zinc Co. research test fence at Palmerton (diluted industrial gases, some zinc oxide).
3	Pyrometer shed, zinc-oxide furnace building (indoor exposure moisture, furnace gases, dust).
5	Directly over furnace, zinc-oxide furnace building (indoor industrial exposure, heat, furnace gases, moisture).
7	Cement crusher building (indoor exposure, raw cement dust).
9	Roof of building in cement manufacturing town (Nazareth, Pa.).
11	Cement-kiln furnace building (indoor exposure, heat, moisture, gases, cement dust).
13	Roof of building in coal-mining town (Lansford, Pa.), near railroad.
15	Coal-breaker building (indoor exposure, moisture, gases).
17	Farm, in low, moist and shaded location near stream, 5 miles southeast of Palmerton.
19	Farm, on hill exposed to sun and wind, 5 miles southeast of Palmerton.
21	Farm, in low, moist location near stream but exposed to sun and wind, 2 miles north of Palmerton.

The monthly inspection consisted of removing dust and *loose* corrosion products by brushing or scrubbing, and determining the change in weight. The surface appearance of the specimens was noted every three months. From the change in weight data corrosion rates in milligrams per square centimeter per month were calculated.

The removal of even loose corrosion products is admittedly questionable. The duplicate undisturbed racks when inspected and weighed at the end of the test will show what effect this procedure may have had.

Sulfur dioxide analyses were made at each location in order to study the effect of the SO_2 content of the atmospheres on the reversal in the order of corrosion resistance noted in the results. The procedure and apparatus described by McKay and Ackerman[1] was used for this purpose.

Experimental Data

Table 1 gives the corrosion rates of the various metals in milligrams per square centimeter per month based on the total change in weight after 11 months' exposure. This is the longest period for which data were available at this writing. After the first six months of exposure the changes in weight from month to month were fairly uniform, so that the data for any month after that give practically the same relative corrosion rate.

Inasmuch as the data are not intended to display a comparison between the metals tested, but to illustrate the vagaries of corrosion, the various materials are designated by letters in the table.

In Table 2, are given the relative order of corrosion rates of the various metals for each location and position of the specimens. In preparing this table a positive corrosion rate was considered as decreasing with increase in the numerical value. For example, the following series of numbers represent low to high corrosion rates: +0.05, +0.02, −0.02, −0.05.

Position 1 in the series represents the lowest corrosion rate and position 9, the highest corrosion rate.

Perhaps this procedure is not justified in terms of absolute corrosion, as a large positive change in weight may imply either great adherence of the corrosion products, which is advantageous, or a high rate of corrosion, which is disadvantageous. It is obvious that there is a difference between a condition that causes a large loss in weight and one causing a gain in weight, but the tabulation serves its intended purpose in pointing out variations in the positions of any metal in the different test locations.

Table 2 also summarizes the results of the sulfur dioxide analyses. The values obtained are the average of from two to five determinations at each location on a clear windy day. Determinations under other atmospheric conditions are not yet available. It is quite certain that under less favorable weather conditions the SO_2 content at most locations would be considerably higher. A determination made at the location of rack 15 shortly after a locomotive had passed through the building showed more than 0.25 p.p.m. of SO_2 as compared with less than 0.05 p.p.m. about an hour later. Likewise, at the location of rack 11 a determination was made close to the base of the stack exhausting the kiln furnace gases, and in spite of a heavy wind 0.10 p.p.m. of SO_2 were found.

[1] R. J. McKay and D. E. Ackerman: Determination of Sulfur Dioxide in Small Amounts in the Atmosphere. *Ind. & Eng. Chem.* (1928) **20**, 538.

TABLE 1.—*Corrosion Rates*
(Milligrams per Square Centimeter per Month)

Metal	Compass Direction	Position	1	3	5	7	9	11	13	15	17	19	21
A	E	V	−0.0212	−0.0435	−0.2480	−0.0035	−0.0126	−0.0018	−0.0524	−0.0014		−0.0144	−0.0112
		H	−0.0194	−0.0308	−0.2230	−0.0034	+0.2560	+0.0083	−0.0404	−0.0364	+0.0009	−0.0055	−0.0227
	W	V	−0.0224	−0.0378	−0.1120	−0.0063	−0.0165	+0.0095	−0.0627		−0.0022	−0.0172	−0.0135
		H	−0.0216	−0.0214	−0.1810	−0.0056	+0.2525	+0.1312	−0.0517	−0.0052	−0.0010	−0.0098	−0.0273
B	E	V	−0.0225	−0.0514	−0.2460	−0.0052	−0.0108	−0.0001	−0.0486	−0.0061	+0.0011	−0.0153	−0.0110
		H	−0.0248	−0.0164	−0.1930	−0.0038	+0.2700	+0.0121	−0.0362	−0.0335	−0.0007	−0.0049	−0.0215
	W	V	−0.0214	−0.0231	−0.0946	−0.0047	−0.0075	+0.0087	−0.0543	+0.0008	+0.0001	−0.0157	−0.0130
		H	−0.0215	−0.0103	−0.1610	−0.0054	+0.2515	+0.1376	−0.0463	−0.0067	−0.0001	−0.0056	−0.0221
C	E	V	−0.0206	−0.0410	−0.2785	−0.0042	−0.0124	+0.0006	−0.0448	−0.0057	+0.0021	−0.0149	−0.0110
		H	−0.0250	−0.0280	−0.2437	−0.0021	+0.2775	+0.0111	−0.0344	−0.0387	+0.0014	−0.0029	−0.0304
	W	V	−0.0181	−0.0308	−0.1057	−0.0051	−0.0131	+0.0084	−0.0515	−0.0015	+0.0015	−0.0226	−0.0111
		H	−0.0221	−0.0078	−0.1715	−0.0044	+0.2755	+0.1390	−0.0432	−0.0087	+0.0020	−0.0032	−0.0233
D	E	V	−0.0131	+0.0142	−0.2282	−0.0025	−0.0131	+0.0009	−0.0378	−0.0043	+0.0056	−0.0115	−0.0076
		H	−0.0225	+0.0073	−0.1710	−0.0021	+0.1995	+0.0241	−0.0290	−0.3032	+0.0021	−0.0024	−0.0209
	W	V	−0.0131	+0.0342	−0.0736	−0.0018	−0.0088	+0.0059	−0.0421	−0.0004	+0.0041	−0.0127	−0.0093
		H	−0.0213	+0.0189	−0.1360	−0.0033	+0.2322	+0.1450	−0.0397	−0.0060	+0.0043	−0.0003	−0.0219
E	E	V	+0.0013	+0.0056	+0.0163	−0.0004	+0.0036	+0.0015	+0.0031	+0.0043	+0.0041	+0.0015	+0.0008
		H	+0.0072	+0.0044	+0.0303	+0.0003	+0.2795	+0.0338	+0.0063	+0.0061	+0.0039	+0.0030	+0.0020
	W	V	+0.0012	+0.0073	+0.0031	−0.0001	+0.0049	+0.0041	+0.0010	+0.0040	+0.0016	+0.0014	+0.0002
		H	+0.0098	+0.0072	+0.0144	−0.0001	+0.3025	+0.1446	+0.0035	+0.0043	+0.0050	+0.0030	+0.0015
F	E	V	+0.0330	−0.2840	−1.9550	+0.0142	+0.0196	+0.0043	+0.0115	+0.0315	+0.0049	+0.0206	+0.0144
		H	+0.0284	−0.2628	−1.4320	+0.0056	+0.2580	+0.0044	+0.0031	−0.0060	+0.0030	+0.0126	+0.0031
	W	V	+0.0363	−0.3272	−0.7350	+0.0178	+0.0234	+0.0069	+0.0024	+0.0249	+0.0057	+0.0196	+0.0150
		H	+0.0322	−0.2478	−1.1800	+0.0111	+0.2695	+0.1236	+0.0016	+0.0140	+0.0060	+0.0143	+0.0030
G	E	V	−0.0028	−0.0141	−0.0650	−0.0018	+0.0026	+0.0011	−0.0015	−0.0011	−0.0004	−0.0005	−0.0007
		H	−0.0013	−0.0094	−0.0664	−0.0006	+0.2916	+0.0300	−0.0015	+0.0004	+0.0031	+0.0024	−0.0005
	W	V	−0.0023	−0.0236	−0.0090		+0.0127	+0.0042	−0.0009	+0.0001	−0.0021	−0.0005	−0.0012
		H	−0.0003	−0.0264	−0.0437	−0.0016	+0.3019	+0.1590	−0.0001	+0.0013	+0.0035	+0.0011	−0.0002
H	E	V	−0.0338	−0.0091	−0.2184	−0.0053	−0.0328	−0.0079	−0.0480	−0.0025	−0.0022	−0.0163	−0.0128
		H	−0.0231	−0.0096	−0.2646	−0.0028	+0.2412	+0.0065	−0.0382	−0.0230	+0.0004	−0.0145	−0.0169
	W	V	−0.0385	+0.0273	−0.0930	−0.0067	−0.0067	−0.0014	−0.0700	−0.0002	−0.0036	−0.0242	−0.0186
		H	−0.0341	+0.0155	−0.1470	−0.0010	+0.2767	+0.1440	−0.0553	−0.0005	+0.0005	−0.0161	−0.0234
I	E	V	+0.0208	−0.9520	−1.7375	−0.3940	−1.0090	+0.0566	−0.2400	−0.0760	+0.7948	−0.3960	−0.0292
		H	+0.6480	−1.9375	−1.2100	−0.0965	−0.0550	+0.0605	−0.1770	−1.0260	+0.0288	+0.0204	+0.3190
	W	V	+0.3896	−1.2100	+0.6285	−0.5740	−1.0500	+0.0585	−0.2145	+0.0203	+0.2360	−0.1245	−0.3960
		H	+0.5250	−2.5840	+0.8155	−0.3017	−0.1315	+0.1878	+0.1295	−0.1286	−0.0803	−0.0798	−0.0082

TABLE 2.—*Order of Corrosion Rate*[a]

Rack	Compass Direction	Position of Specimen	1	2	3	4	5	6	7	8	9	SO_2, Parts per Million
1	E	V	F	I	E	G	D	C	A	B	H	Trace < 0.05
		H	I	F	E	G	A	D	H	B	C	
	W	V	I	F	E	G	D	C	B	A	H	
		H	I	F	E	G	D	B	A	C	H	
3	E	V	D	E	H	G	C	A	B	F	I	
		H	D	E	G	H	B	C	A	F	I	0.15
	W	V	D	H	E	B	G	C	A	F	I	
		H	D	H	E	C	B	A	G	F	I	
5	E	V	E	G	H	D	B	A	C	I	F	
		H	E	G	D	B	A	C	H	I	F	1.70
	W	V	I	E	G	D	H	B	C	A	F	
		H	I	E	G	D	H	B	C	A	F	
7	E	V	F	E	G	D	A	C	B	H	I	
		H	F	E	G	D-C	D-C	H	A	B	I	0.05
	W	V	F	G	E	D	B	C	A	H	I	
		H	F	E	H	G	D	C	B	A	I	
9	E	V	F	E	G	B	C	A	D	H	I	
		H	G	E	C	B	F	A	H	D	I	None detected
	W	V	F	G	E	H	B	D	C	A	I	
		H	E	G	H	C	F	A	B	D	I	
11	E	V	I	F	G	G	D	C	B	A	H	
		H	I	E	G	D	B	C	A	H	F	Trace < 0.05
	W	V	I	A	B	C	F	D	G	E	H	
		H	I	G	D	E	H	C	B	A	F	
13	E	V	F	E	G	D	C	H	B	A	I	
		H	E	F	G	D	C	B	H	A	I	Trace < 0.05
	W	V	F	E	G	D	C	B	A	H	I	
		H	I	E	G	F	D	C	B	A	H	
15	E	V	I	F	E	G	A	H	D	C	B	
		H	E	G	F	H	B	A	C	D	I	> 0.05 < 0.10
	W	V	F	I	E	B	G	A	H	D	C	
		H	F	E	G	H	A	D	B	C	I	
17	E	V	I	D	F	C	E	B	A	G	H	
		H	I	E	G	F	D	A	A	H	B	None detected
	W	V	I	F	D	E	C	B	G	A	H	
		H	F	E	D	G	C	H	B	A	I	
19	E	V	F	E	G	D	A	C	B	H	I	
		H	I	F	E	G	D	C	B	A	H	None detected
	W	V	F	E	G	D	B	A	C	H	I	
		H	F	E	G	D	C	B	A	H	I	
21	E	V	F	E	G	D	B-C	B-C	A	H	I	
		H	I	F	E	G	H	D	B	A	C	None detected
	W	V	F	E	G	D	C	B	A	H	I	
		H	F	E	G	I	D	B	C	H	A	

[a] Specimens showing a gain in weight were considered as having a low corrosion rate; the greater the gain, the lower the rate, and vice versa. Furthermore, in studying this table it should be remembered that the order was determined by change in weight only.

DISCUSSION OF RESULTS

It is evident from Table 2 that in only a few exposures did the metals fall in the same order of endurance. It is true that the differences were at times small but the differences will undoubtedly be accentuated as the test continues.

Five of the nine metals occupy position 1 at one exposure and positions 8 and 9 in other exposures. In other words, five of the nine metals are capable of forming adherent corrosion products under certain conditions of exposure and nonadherent products under other conditions.

Under a third set of conditions the same metals will undergo practically no corrosion. This point is particularly well illustrated by the behavior of metal I. For convenience, the weight changes for this metal are summarized in Table 3.

TABLE 3.—*Summary of Weight Changes of Metal I*

Rack Number	Location	Position	Weight Changes, Mg. per Sq. Cm. per Month	
			East	West
1	Palmerton	Vertical	+0.0208	+0.3896
		Horizontal	+0.6480	+0.5250
3	Oxide-furnace building pyrometer shed.	V	−0.9520	−1.2100
		H	−1.9375	−2.5840
5	Oxide-furnace building over oxide furnace.	V	−1.7375	+0.6285
		H	−1.2100	+0.8155
7	Cement crusher building	V	−0.3940	−0.5740
		H	−0.0965	−0.3017
9	Cement manufacturing town	V	−1.0090	−1.0500
		H	−0.0550	−0.1315
11	Cement-kiln building	V	+0.0566	+0.0585
		H	+0.0605	+0.1878
13	Coal-mining town	V	−0.2400	−0.2145
		H	−0.1770	+0.1295
15	Coal-breaker building	V	+0.0760	+0.0203
		H	−1.0260	−0.1286
17	Moist, shady, rural	V	+0.7948	+0.2360
		H	+0.0288	−0.0803
19	Dry, sunny, rural	V	−0.3960	−0.1245
		H	+0.0204	−0.0798
21	Moist, sunny, rural	V	−0.0292	−0.3960
		H	+0.3190	−0.0082

While it is not the writer's intention to offer explanation for the variations noted in this work, it is interesting to note that metal F occupied a position indicating a high corrosion rate only in the atmospheres high in SO_2. This is the only connection detected between the SO_2 content of the atmosphere and the type or rate of corrosion.

The variations between specimens exposed in opposite positions and directions are noteworthy.

In conclusion, the writer wishes to point out again that these data are presented only to indicate the grave difficulties connected with the development of an accelerated atmospheric weathering test for metals which will give indicative results for a variety of atmospheric conditions.

ACKNOWLEDGMENT

The writer acknowledges with pleasure the cooperation of W. M. Peirce in planning the work and of W. Hammel in making the tedious necessary weighings.

Addendum

The results of similar tests on racks exposed in various parts of the United States in a variety of atmospheres strongly confirm the data presented in the paper and show that the widely varying results noted in the Lehigh Valley exposures, after 11 months of exposure, may reasonably be expected after a longer period of exposure.

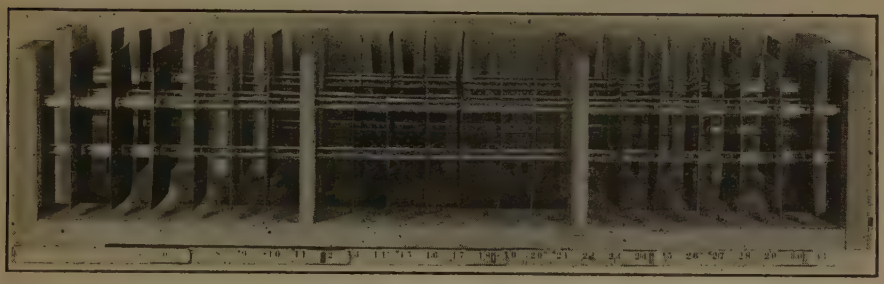

Fig. 3.—Side view of assembled test rack used outside the Lehigh Valley.

Table 4.—*Corrosion Rate over Longer Period of Exposure*
Milligrams per Square Centimeter per Month for 3 Years

Metal	Palmerton	New York	Montauk	Pittsburgh	Hanover, N. M.	Key West
J	+0.0333	−0.0498	+0.0118	+0.0318	−0.0011	+0.0467
K	−0.0734	−0.4160	−0.0511	−0.2670	−0.0053	−0.0069
L	−0.0305	−0.1582	−0.0305	−0.0742	−0.0043	−0.0019
E	+0.0063	+0.0753	+0.1790	+0.0453	+0.0008	+0.0179
M	−0.0045	−0.0947	−0.0043	−0.0616	−0.0013	+0.0261
N	+0.0120	−0.0731	−0.0058	−0.0367	−0.0009	−0.0343
A	−0.0417	−0.2255	+0.0203	−0.1665	−0.0030	+0.1935
B	−0.0328	−0.2002	+0.0393	−0.1105	−0.0023	+0.2118
F	+0.0396	−0.0681	−0.0017	−0.0338	−0.0003	+0.0597
O	+0.0015	+0.0085	−0.0820	+0.0026	−0.0054	+0.0723
P	−0.0497	−1.1810	+0.0358	−0.1270	−0.0094	+0.0553
Q	+0.0226	+0.0124	+0.0296	+0.0068	−0.0010	+0.1098
R	−0.0553	−2.4480	−0.0314	−0.2701	−0.0126	+0.1031
H	−0.0698	−0.3075	+0.0148	+0.1895	−0.0077	+0.2265
S	+0.0116	+0.0159	−0.0375	+0.0118	−0.0012	+0.0528
I	−0.2425	−2.2250	−1.2470	−1.3730	−0.0822	−0.1725
T					−0.1543	−0.4750
G	−0.0036	+0.0173	+0.0119	+0.0047	−0.0097	+0.1777

A different type of rack was used for these tests (Fig. 3). Eighteen different types of metals were exposed in duplicate. One rack was exposed at each of the following locations:

1. New York, N. Y. (salt-industrial atmospheres)
2. Pittsburgh, Pa. (severe industrial atmospheres)
3. Montauk Point, L. I., N. Y. (northern salt atmospheres)
4. Key West, Fla. (southern salt atmospheres)
5. Hanover, N. M. (dry pure atmospheres)
6. Palmerton, Pa.

Corrosion rates in milligrams per square centimeter per month are given in Table 4. In Table 5 the metals have been arranged in the order of corrosion for each location.

TABLE 5.—*Order of Corrosion* (3 *Years*)

Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Palmerton, Pa.	F	J	Q	N	S	E	O	G	M	L	B	A	P	R	H	K	I	T
New York, N. Y.	E	G	S	Q	O	J	F	N	M	L	B	A	H	K	P	I	R	T
Montauk, N. Y.	E	B	P	Q	A	H	G	J	F	M	N	L	R	S	K	O	I	T
Pittsburgh, Pa.	E	J	S	Q	G″	O	P	N	M	L	B	P	A	H	K	R	I	T
Hanover, N. M.	E	F	N	Q	J	S	M	B	A	L	K	O	H	P	G	R	I	T
Key West, Fla.	H	B	A	G	Q	R	O	F	P	S	J	M	E	L	K	N	I	T

DISCUSSION

N. B. PILLING, Bayonne, N. J.—There has not been much published dealing particularly with atmospheric corrosion tests except for steels, and the author is to be commended for emphasizing the difficulties not only of measurement but of interpretation involved in this perplexing subject.

My first criticism concerns the suppression of the identity of the metals he has worked with. He tells us what in general is included, and it appears that quite a range is covered, including sheet iron, copper, zinc, stainless steel and some others. I wonder if we are yet ready, with the present stage of development in corrosion testing, and of atmospheric corrosion tests in particular, to consider these tests in the abstract way required by the suppression of identity. Valuable as the results are which the author gives, we are left somewhat in the position of a student of the famous blindfold test—if we wish to carry our study of the author's data beyond his general conclusion there is no alternative but to start all over and repeat the entire experiment ourselves. One requirement of a scientific paper is that it should so state things that anyone wishing to pursue the subject further may start where it leaves off. It is hoped that in his final report the author will feel greater liberty in this regard.

My second point deals with the method of interpretation. The author rates his specimens by assuming that those with the greatest increase in weight have corroded least, while those with the greatest loss in weight have corroded most. That is, as I understand it, a steel sheet which had rusted profusely yet retained the rust coating adherently would be considered to have a low rate of corrosion. If, on the other hand, a plate of glass or some other substance that was not attacked at all by the atmosphere had been included and rated with the other specimens, it would fall somewhere in the middle of the series, with an indicated corrosion rate greater than the steel just mentioned. This indicates, of course, that not only must an adequate method of measuring corrosion be arranged, but that a good deal of judgment must be used in its interpretation.

If the data given in Table 1 are rearranged giving the order of merit of the various metals and following the general scheme of Table 2, but basing the analysis on this

assumption, that those specimens which have changed most in weight—whether an increase or a decrease—have corroded most, the more paradoxical conclusions of the paper may be somewhat modified. In place of the condition summarized at the bottom of page 285, "Five of the nine metals occupy position 1 at one exposure and positions 8 and 9 in other exposures," it will be found that the metals designated E and G occupy first position (least corrosion) in 75 per cent. of the cases, and the same two metals occupy second position in 55 per cent. of the cases, whereas metal I which is particularly used to illustrate the wide vagaries of corrosion, occupies last, or next to the last place, in 91 per cent. of the cases.

C. L. Hippensteel, New York, N. Y.—It seems to me that this paper is doing in large measure what it sets out to do; that is, to show that the problem of establishing the universal accelerated corrosion test will be very difficult. The environment of atmospheric exposure is so complicated and variable that it will be difficult, if at all possible, to establish a given set of conditions that will illustrate corrosion under all circumstances. This seems to indicate the necessity for a great deal more theoretical investigation of the factors in atmospheric exposure that have a pronounced effect in producing corrosion, and after those are ferreted out, the use of them in the accelerated test.

It further illustrates the difficulty of attempting to judge corrosion by weight-loss measurements alone. While it is true the increase in weight due to corrosion film formation will so complicate the results that it is hardly advisable to rate metals on weight change basis alone, it will be difficult to attempt to do with a large number of metals what Mr. Friend and others have done in England; that is, to take into account in the weight change measurements, the amount of corrosion products retained on the surface and those lost, namely "surrosion" and "errosion" products. While it is true that the weight-loss measurements do not give an extremely accurate statistical measure of the weight of corrosion, it has been our experience on some preliminary tests on corrosion of steel and non-ferrous metals in outdoor exposure that there was a definite very marked loss in weight of iron over other metals that were included in the test, despite the formation of a thick oxide film formation on the iron. Where there are marked differences in rate of corrosion, in a qualitative sense, weight-loss measurements may be of value. Along the line of inconsistencies of results that may be obtained, one case came to our attention recently on some stainless steels. They were exposed on a rack at a 45° angle. The full area of the front of the plate was exposed, and about two-thirds of the back. The samples were also exposed to a periodic spray, and judging corrosion from a visual standpoint (we were interested particularly in the staining or film that would form), apparently the most serious corrosion was on the under side of the samples rather than on the upper side where the spray struck them.

The paper certainly illustrates the difficult problem of applying our corrosion information (laboratory or theoretical) in a practical way in choosing the right metal for a specific application.

W. H. Finkeldey, New York, N. Y.—It is only natural that one should become confused when examining loss or gain in weight data secured from corrosion test specimens that have been exposed only a short period of time in the atmosphere. The author is to be commended for attempting to present his report at this stage of his tests.

However, it is well to keep in mind that the process of corrosion will ultimately straighten out this situation. In another 5 or 10 years it will be readily apparent which specimens are corroding most rapidly and by that time it will not be necessary to determine the extent of corrosion from any consideration of gain in weight data.

This test is only in its earliest stages and ultimately all specimens will show a loss in weight.

If it were possible to inspect the specimens themselves while considering the corrosion data, a much better picture of what has taken place would be secured. The importance of this feature has been recognized by Committee B-3 of the American Society for Testing Materials, which is starting, this year, a series of atmospheric corrosion tests on a wide variety of non-ferrous metals. The plan is to exhibit the test specimens whenever they are brought in from the test locations for the determination of loss in weight data. This will permit those interested in the tests to secure a much better idea of the corrosion that has taken place in the various atmospheres than would be possible from the bare consideration of loss or gain in weight data.

When his specimens have undergone more weathering, I hope the author will present another paper telling the story of what has taken place in the interval. It would be helpful if he could present the data together with some low-power photographs of the surface of the specimens, which should give some picture of the type of corrosion and the character of surface films formed by the products of corrosion. It would also be helpful, as Mr. Pilling has suggested, to reveal the identity of the test specimens.

C. E. Reinhard (written discussion).—Mr. Pilling and Mr. Finkeldey have both questioned the omission of the identity of the samples tested. The writer would again emphasize that the data are advanced solely for the purpose of indicating the wide range of results which can be obtained in a limited geographical area, and so pointing out one of the difficulties in the way of developing a universal accelerated test.

Further analysis of the data would, in the author's opinion, be fruitless. When periodic readings over a number of years are available, such analysis will be important.

The interpretation of corrosion by means of change in weight data is admittedly open to question unless substantiated by other observations, such as were used in this case, though perhaps not clearly pointed out in the paper. The entire subject of the paper is summed up in one point; namely, that an accelerated test designed to study the corrosion of a metal (I, for example) would have to be extremely versatile in order to predict this experience.

Smoothing and Etching Cupronickel, Bronze, Brass and Steel

By H. B. Pulsifer,* Cleveland, Ohio

(Philadelphia Meeting, October, 1928)

This paper outlines a method for rapid production of flat, granular surfaces on many of the medium hard alloys. Grinding wheels and fabrics on wheels are not used; the purpose is accomplished by rubbing on emery papers and on fine abrasives heaped on hand boards. The advantages of chromic acid in the solutions for etching nickel and copper alloys are explained. Steels may require an additional step in the mechanical smoothing owing to the lack of an ideal etchant. Chloric acid is a rapid etchant for steel. Thirty-six photomicrographs illustrate the steps in smoothing and the clearness with which structures can be rapidly exposed. New structures in low-carbon steels are announced. After a little practice, many materials can be finished within two or three minutes.

Cupronickels

In the previous papers on the metallography of copper and magnesium which the author has presented to this Institute there has been an attempt to demonstrate the advantages of minimizing the mechanical work of surfacing and depending more on chemical means; the present paper continues the research into a still wider field.

It is obvious that the success of a chemical method for smoothing and etching depends almost entirely on the use of a suitable reagent. The etchant must remove the surface granulations and outline the structures. A very special type of reaction between reagent and metal must be displayed. Promiscuous corrosion or the intensification of the attack about local couples formed by impurities or components must not be in evidence.

There are several reagents that etch highly polished nickel and copper alloys very well. Acidified ferric chloride solutions, concentrated and dilute nitric acid solutions, and nitric and acetic acids in acetone have been used to good advantage for the purpose. However, if they are expected to etch rather deeply—that is, smooth as well as characterize—the results may be far from satisfactory.

Advantages of Chromic Acid

In a protracted series of experiments it has been found that the addition of chromic acid may be of the most surprising benefit. The function

* Metallurgist, Ferry Cap & Set Screw Co.

of the chromic acid is to render the metal more passive to chemical attack. Only major features come into relief. Local couples and corrosion pits fail to develop. Crystals come into relief by virtue of their relative rate of solution over an entire exposed section. It is a dissolving dependent on the different rates of solution as determined by the crystallographic section exposed. Incidentally, two crystals in contact and with all axes parallel or with sections dissolving at the same rate fail to yield a bold line of demarcation. Bold and faint crystal boundaries characteristically appear on many of the prints.

When a piece of smoothed monel metal sheet is etched with concentrated nitric acid containing chromic anhydride the result appears as in Fig. 1. This sheet is 20 hard by the scleroscope; it was etched 20 sec. in the reagent.

Nitric acid alone had been found to differentiate crystal borders very well but to dissolve the matrix excessively about inclusions. The idea of adding the chromic acid came directly from the known effect of powerful oxidizing agents rendering metal passive. Incidentally, the function of chromic acid in the Palmerton solution for etching zinc was in mind. It was strongly perceived that the Palmerton reagent contains chromic acid to render the metal passive while the sulfuric acid selectively etches only the chief structural boundaries. We all recall that comparatively few photomicrographs portrayed the structure of zinc before the announcement of the Palmerton reagent. That was a very important disclosure in 1919 in the paper by Mathewson, Trewin and Finkeldey.[1]

Chromic acid has often been used as a component of etching solutions, notably for etching silver. Mr. Vilella, of the Union Carbide and Carbon Research Laboratories, found chromic and hydrochloric acids splendid etchants for certain copper alloys.[2]

Mechanical Smoothing

It should be explained that the present report on the use of etchants is concerned with their use as smoothers as well as grain developers. No real polishing of the metal surface is attempted. A granular surface has to be cleared and underlying features delineated.

A specimen that has been reduced to suitable size by the usual hacksaw method may be conveniently filed fairly level in a vise. It is then dragged across a flat mill file laid on a bench until the surface has one facet and has been planed to the corners. The file should be of medium fineness. It is essential to obtain one single facet for the subsequent operations are brief and not suited to removing much metal.

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[1] C. H. Mathewson, C. S. Trewin and W. H. Finkeldey: Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. *Trans.* (1920) **64,** 305.

[2] J. R. Vilella: Delving into Metal Structures. *Iron Age* (1926) **117,** 834.

The filed specimen is then rubbed on No. 0 coarse emery paper on a piece of plate glass until the deepest file scratches have disappeared. This is a quick operation and it is not necessary to change the direction of abrasion.

The next step is to rub the specimen on No. 0 fine emery paper to remove the metal to a new and finer surface. This, also, requires only a few seconds. A surface of monel metal will appear as in Fig. 2 at 100 diameters.

The specimen is then rubbed on No. 000 fine emery paper until the surface is entirely reduced to the newer and finer set of striations. Fig. 3 shows the characteristic appearance at this stage.

The next steps of the smoothing are done on damp abrasive heaped on chamois skin stretched over a paraffined board. Carborundum powder (washed, 6 min.) is on one board and washed ground tripoli on the other.

Each abrasive is moistened only enough to hold together and support the specimen under pressure. The specimen should never touch the underlying chamois skin.

The specimen is rubbed on the carborundum powder only a few seconds. Care is taken to rub all parts of the surface and enough pressure is used to insure rapid removal of metal. The appearance of the surface after a few seconds is shown in Fig. 4, at 100 diameters.

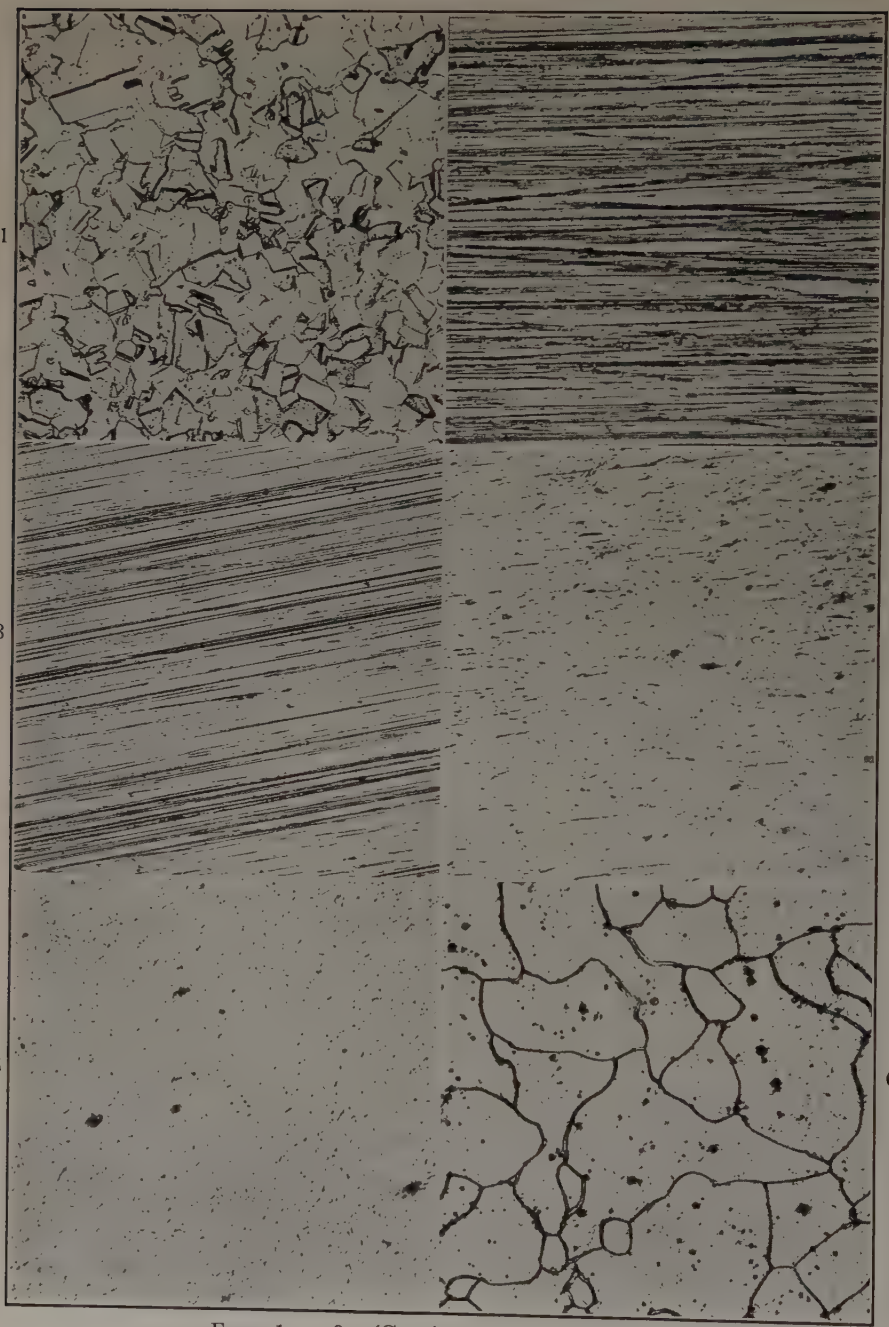
The final step of the mechanical smoothing is a repetition of the last process but carried out on the other board, which has a heap of moistened tripoli powder. Since the tripoli powder is light colored it is possible to gage the amount of the abrasion by the blackening of the tripoli. Rapid blackening of the powder assures one of rapid smoothing. After a few seconds' work the surface should appear about as in Fig. 5.

The last two rubbings have largely eliminated scratches and they have been brief enough to leave the surface level. The surface is not polished and glassy but granular.

Etching Cupronickels

If a surface prepared as indicated is agitated for a few seconds in concentrated nitric acid containing chromic anhydride, the structure should appear as well as the one shown in Fig. 1. The depth of the etching can be varied within rather wide limits without harmful pitting or unequal dissolving.

It will be found that a first light etch and repolish on the tripoli before a final etching is highly advantageous. The attack of the acid gives a fresh tooth to the tripoli. The abraded metal seems to impregnate the powder and assist in making the surface smooth. The repolishing delays the work only slightly. Careful repolishing one or more times gives



FIGS. 1 TO 6. (Captions on opposite page.)

superior surfaces free from the wavy grooves that are residual after earlier strains from filing or the coarser emery papers.

With a little practice it would probably be possible to prepare most of the surfaces shown in this paper in a finishing time of about two minutes each, and any of them in less than four minutes. This means the time required on the emery papers, the carborundum and tripoli, and the etching.

It is well known that annealed metal usually etches more clearly than cast or heavily cold-worked material. The nitric and chromic acids etch cupronickels well, whatever their condition.

Fig. 6 shows the results obtained on a cast, soaked and quenched monel metal. The finer network of lines so prominent in the cast and heavily cored condition are only faintly visible. Although numerous inclusions are present the metal has not been unduly dissolved about them.

The strained metal in the threaded section of a roll-threaded monel metal cap screw is shown in Fig. 7. This surface has been heavily etched but holes do not appear about the inclusions as when other etchants are used.

Fig. 8 shows the metal flow in the thicker portion of the roll thread but more lightly etched. The slippage and elongation of the crystals is plainly seen.

In similar manner, the structure of the metal in the heads of cold upset cap screws or in sheets that have been cold-rolled is much more clearly portrayed with the new reagent than with any of the others commonly used.

A final print on the cupronickels is given in Fig. 9. This is the usual appearance of a longitudinal section through Mond-70 annealed wire 0.368 in. dia. The longitudinal striations are considerably more numerous than in monel metal.

Bronzes and Brasses

Most of the copper alloys disclose their structures fairly well when attacked by a variety of reagents. The voluminous literature on the subject is well illustrated with excellent prints. Yet the extreme simplicity and ease of surfacing without wheels or moving fabrics justifies

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Fig. 1.—Annealed sheet monel metal. Etched 20 sec. in conc. $HNO_3 + CrO_3$. × 100. Scleroscope hardness = 20.

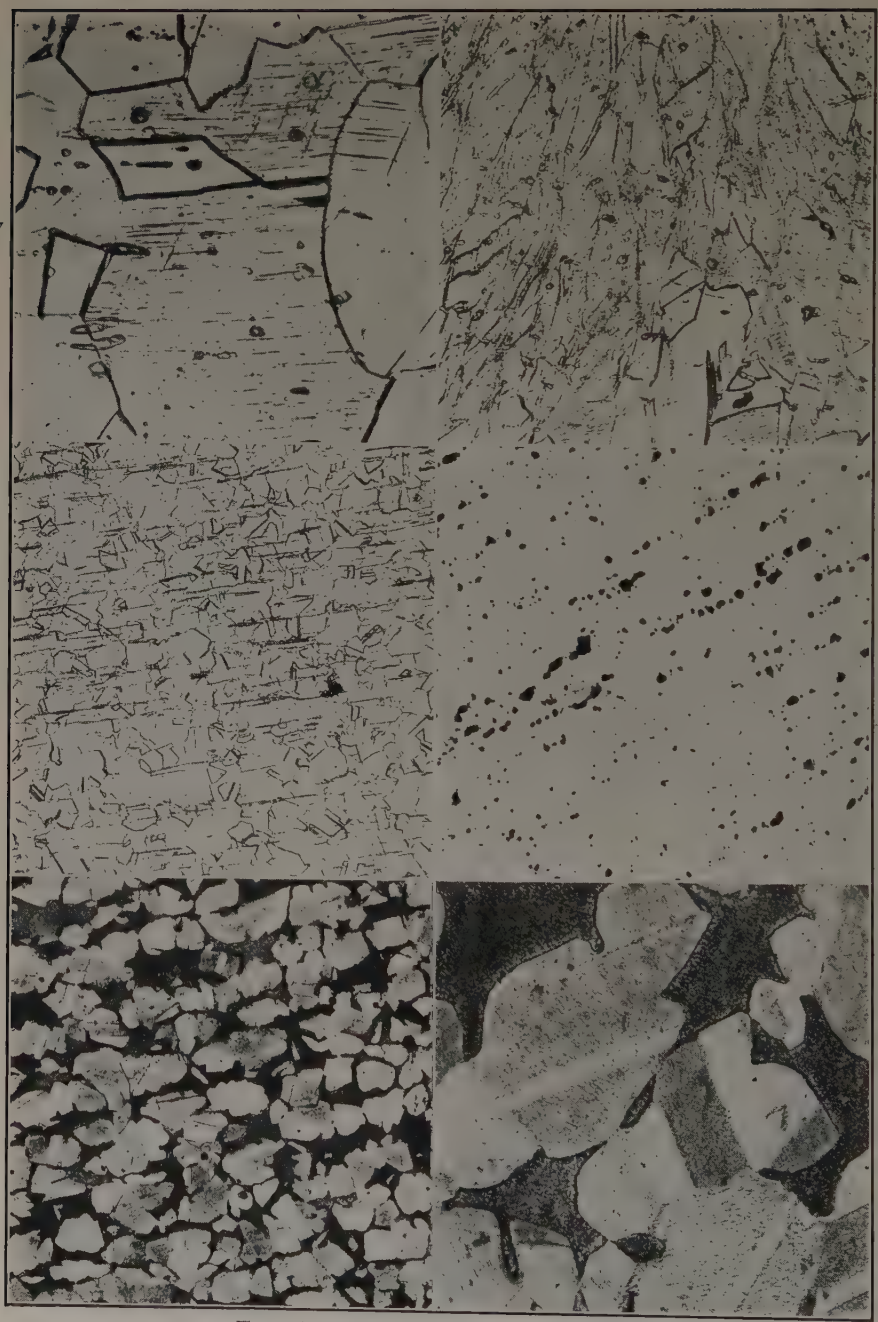
Fig. 2.—Sheet monel metal, smoothed with No. 0 fine emery paper. × 100.

Fig. 3.—Sheet monel metal, smoothed on No. 000 fine emery paper. × 100.

Fig. 4.—Sheet monel metal, smoothed on carborundum powder heaped on a hand board. × 100.

Fig. 5.—Sheet monel metal, smoothed on tripoli powder heaped on a hand board. × 100.

Fig. 6.—Cast monel soaked at a red heat and quenched. Etched with conc. $HNO_3 + CrO_3$. × 100.



FIGS. 7 TO 12. (Captions on opposite page.)

mention. There is also a possibility that the use of chromic acid as a component of etchants may find general application.

Ground and washed tripoli appears to be an ideal abrasive for the final mechanical smoothing of these medium hard alloys. Specimens of bronze and brass rub out to an almost scratch-free and finely granular surface in a very few seconds. These alloys are neither too soft, so that they deform, nor too hard, so that they fail of rapid erosion to a flat granular surface.

The procedure is exactly the same as with cupronickels. If it is intended to finish a smooth surface without etching it is well to etch slightly and give a final smoothing on the tripoli. This leaves a surface suitable for observing inclusions, defects, hard and soft components.

A good example of the results that may be attained is at hand in the case of a brass that contained too much lead to cold-head without shearing. This brass, which contained 3.5 per cent. lead, is shown in Fig. 10 at 100 dia. It is a longitudinal section with the final smoothing on tripoli. The black spots are the globules of lead. Hardly over two minutes is required to prepare a surface in the manner just described.

Bronze Wire

A Tobin bronze wire sheared instead of flowed plastically when subjected to cold-heading. This bronze had very nearly the chemical composition of other material that headed well. Microscopical examination showed a large amount of the hard beta component. The material smoothes readily and discloses its main structural features with several reagents. A light etch with ammonium persulfate solution develops the beta as a white constituent forming spider-web areas between the rounded alpha crystals. Concentrated nitric acid outlined the grain borders in very low relief but failed to differentiate clearly the two constituents.

The most satisfying result was obtained by dipping the specimen in concentrated nitric acid and washing, then dipping for a moment in acid ferric chloride solution. The first dip gave a glossy surface with hair-fine delineations; the second dip colored the beta dark and made the twinnings on the alpha grains more prominent. This experiment succeeded so well that prints are given at both 100 and 500 diameters.

FIG. 7.—STEM OF MONEL METAL CAP SCREW. ETCHED WITH CONC. $HNO_3 + CrO_3$. $\times$ 100. SCLEROSCOPE HARDNESS = 28.

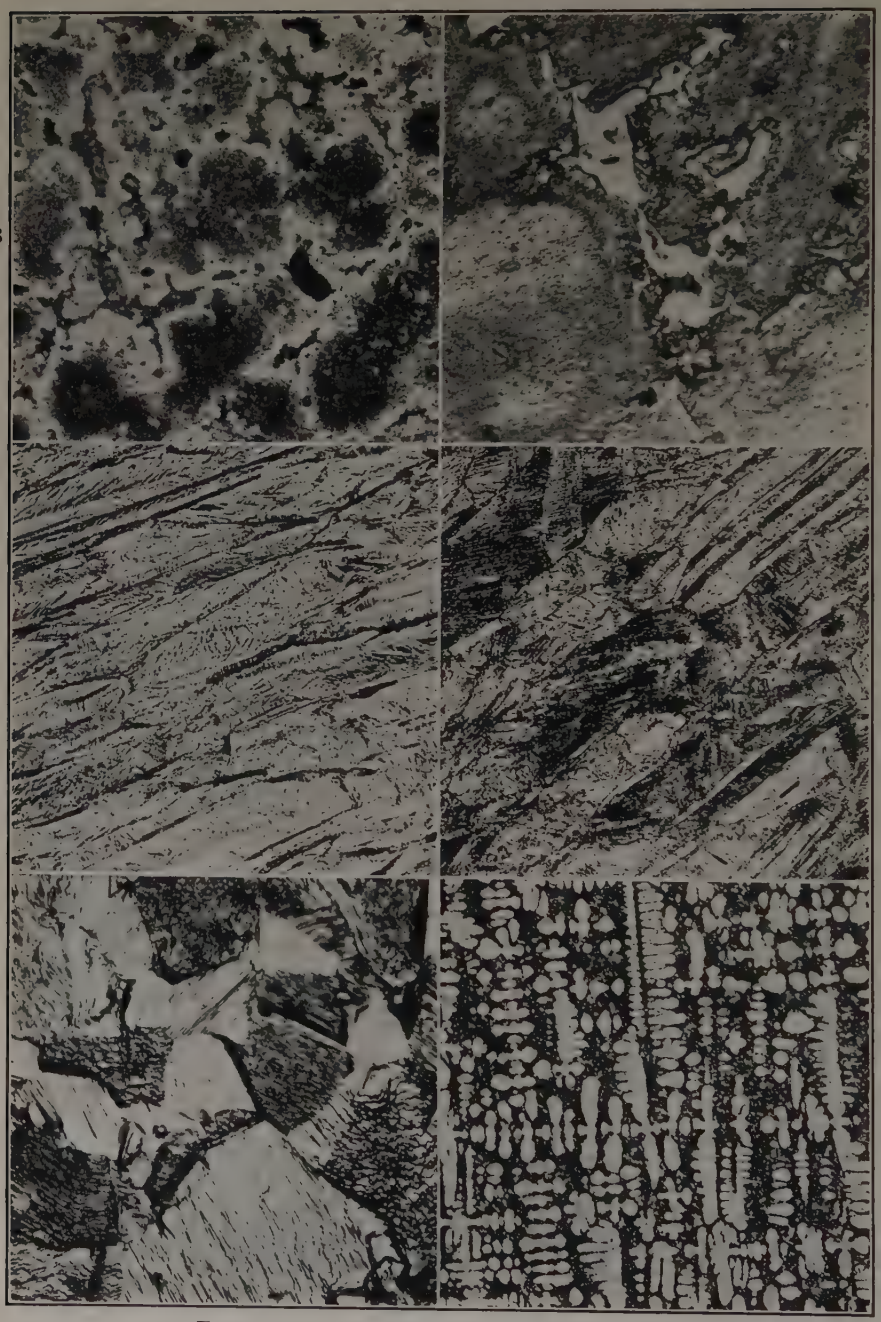
FIG. 8.—SECTION THROUGH ROLL THREAD OF MONEL METAL CAP SCREW. ETCHED WITH CONC. $HNO_3 + CrO_3$. $\times$ 100.

FIG. 9.—MOND-70 WIRE, 0.368 IN. DIA. ETCHED WITH CONC. $HNO_3 + CrO_3$. $\times$ 100. SCLEROSCOPE HARDNESS = 19.

FIG. 10.—LEADED BRASS, SMOOTHED ON TRIPOLI. NOT ETCHED. $\times$ 100.

FIG. 11.—TOBIN BRONZE, ETCHED 1 SEC. IN CONC. HNO_3 AND 1 SEC. IN SPECIAL $FeCl_3$ SOLUTION. $\times$ 100. SCLEROSCOPE HARDNESS = 20.

FIG. 12.—TOBIN BRONZE. $\times$ 500. SAME AS FIG. 11.



FIGS. 13 TO 18. (Captions on opposite page.)

The special acid ferric chloride solution used for the etching was made up as follows: water, 100 ml.; HCl (conc.), 1 ml.; $FeCl_3$ (solid), 10 g.; CrO_3 (solid), 1 g. This solution, containing chromic acid to render the metal more passive, appears to be an excellent reagent for etching many of the more complex bronzes.

Special Bronzes

An art bronze only 12 hard by the scleroscope contained numerous hard particles that made the finishing of statuettes too difficult (Fig. 13). This bronze contains 4.0 per cent. lead and besides the soft globulites, which are mainly lead, there are at least three hard components that are in evidence the moment one attempts to cut the material.

Certain minute but extremely hard and brilliant crystals smooth in very high relief in a black, globular constituent. They are probably tin oxide. The black constituent is hard and smoothes poorly on the tripoli. The usual bright delta component is hard and maintains its scratches in spite of rubbing on tripoli. A magnification of 1000 dia. is suitable to characterize these minor components. Fig. 13 indicates the cored dendritic features and the complexity of the alloy.

A bronze used for bearing purposes is shown in Fig. 14. This alloy has its delta component augmented and hardened with nickel. This is a phosphor-nickel bronze. Mr. Bierbaum, of the Lumen Bearing Co., has determined the relative hardness of the matrix and the delta component. His micro-character hardness tester determines the delta as 750 hard; the matrix is only 75 hard. This alloy reveals its characteristics in many reagents but in none better than in the special ferric chloride etchant.

Phonoelectric bronze is one of the solid-solution alloys available for cold-heading purposes. Even when partly tempered by cold-drawing it is plastic enough to head well. It has very much the appearance of pure copper, but cap screws made of it have a tensile strength of 75,000 lb. per sq. in. Fig. 15 shows the elongated crystals in the wire after etching with nitric acid containing chromic acid.

FIG. 13.—ART BRONZE, ETCHED IN SPECIAL $FeCl_3$ SOLUTION. × 200. SCLEROSCOPE HARDNESS = 12.

Copper	86.0 per cent.	Tin	7.9 per cent.
Zinc	2.1 per cent.	Lead	4.0 per cent.

FIG. 14.—PHOSPHOR-NICKEL BRONZE. ETCHED WITH SPECIAL $FeCl_3$ SOLUTION. × 500. SCLEROSCOPE HARDNESS = 22.

Nickel	3.5 per cent.	Tin	10.6 per cent.
Lead	2.5 per cent.	Phosphorus	0.06 per cent.

FIG. 15.—PHONOELECTRIC ALLOY WIRE, 0.368 IN. DIA. ETCHED WITH CONC. HNO_3 + CrO_3. × 200. SCLEROSCOPE HARDNESS = 26.

FIG. 16.—EVERDUR BRONZE WIRE, 0.265 IN. DIA. ETCHED WITH SPECIAL $FeCl_3$ SOLUTION. × 100. SCLEROSCOPE HARDNESS = 37.

FIG. 17.—COPPER WITH 1.7 PER CENT. BERYLLIUM. HOT-FORGED, 17 SCLEROSCOPE. ETCHED WITH CONC. HNO_3. × 500.

FIG. 18.—CUPRONICKEL WITH 5 PER CENT. BERYLLIUM. ETCHED WITH SPECIAL FERRIC CHLORIDE SOLUTION AND SLIGHTLY REPOLISHED. × 100. BRINELL HARDNESS = 302.

Everdur is another solid-solution bronze that is strong and plastic. Cap screws made of it may have a strength of 90,000 lb. per sq. in. Fig. 16 is a print of wire suitable for cold-heading. This wire is 37 hard by the scleroscope and shows heavily worked and elongated crystals. The strain markings and twinnings confuse the structure yet the crystals are fairly well distinguished by the special ferric chloride etchant.

Beryllium Bronzes

The beryllium bronzes etch readily in several reagents. They become possibly too shiny and glassy in concentrated nitric acid containing chromic acid. They respond to plain concentrated nitric acid in the superb way that pure copper does.

Fig. 17 shows a hot-forged beryllium bronze containing 1.7 per cent. beryllium. This was etched with concentrated nitric acid. The beta component that was prominent in the cast alloy has been practically all absorbed. The material greatly resembles pure hot-forged copper but is 17 hard by the scleroscope.

Cupronickels that have been modified by the addition of beryllium present a very distinctive and highly interesting series of alloys. Fig. 18 shows such an alloy containing 5 per cent. beryllium. This alloy is in the cast condition. It was etched with the special ferric chloride solution and very gently rubbed on tripoli to whiten the alpha dendrites. Cupronickel is noticeably resistant to chemical attack but this alloy responds instantly. Higher magnification easily resolves the dark ground of Fig. 18 into a beautiful eutectic, which is highly susceptible of alteration by heat treatment. Incidentally, the addition has raised the hardness of the cast alloy from Brinell 126 to Brinell 302.

Alpha Brasses

As might be expected, the single-phase alpha brasses rub to a granular surface very easily and with copious black smudge. Their crystals are brilliantly outlined by either color boundaries or line boundaries.

The brass shown in Fig. 19 has been etched with hydrogen peroxide in concentrated ammonia solution. The brass shown in Fig. 20 was etched in concentrated nitric acid containing chromic anhydride. Two or three minutes is required to finish material of this sort for photographing.

Excellent results are obtained by a dip in concentrated nitric acid and then a dip in ferric chloride solution or a few seconds in ammonia and peroxide.

Steels

The etching of many varieties of steel presents a more difficult problem than numerous non-ferrous metals and alloys.

Most fundamental of all, there appears to be no etchant that will attack pure iron and its solid-solution alloys as selectively and uniformly as an ideal reagent should. A dozen reagents will clear a granular surface of magnesium and then uniformly and clearly reveal the chief structural features. It is doubtful if a single similar reagent is known for iron.

Steel that contains pearlite and ferrite is easily overetched in the pearlitic areas before the crystal boundaries of the ferrite appear clearly.

The problem of surfacing rapidly apparently is further complicated in many instances by globulites of cementite dislodging and scoring the ferrite during the rubbing. The globulites of cementite may remain embedded in a totally false position.

Tripoli is too soft for very hard metal but this may be partly overcome by light etching and repolishing.

However, many ferrous materials do finish rapidly and well. More than likely other workers will devise a technique that will fit all cases. The photomicrographs were obtained, of course, by abbreviating the mechanical work and without the use of wheels or fabrics.

The slightly granular surface left by rubbing on tripoli far from precludes a study of the defects and inclusions in certain materials. Thus, in Fig. 21, the slightly granular surface is not entirely scratch-free yet the spot of slag and numerous faint dots of oxide are given in tolerably clear outline. This is a piece of ingot iron.

When this surface is lightly etched with nitric or picric acid in alcohol the scratches largely disappear and grain borders begin to appear before pitting occurs about the dots of oxide. Another piece of ingot iron, Fig. 22, prepared in a similar way, showed numerous very hard and angular crystals embedded in globular drops of oxide. Since the section of the hard crystals is slightly higher than the general level of the metal, it was necessary to focus on the crystals rather than on the metal. This leaves the metallic surface slightly blurred.

It is also understood that the granulations may be softened, as with conical illumination, or intensified by using pinhole illumination.

There is one more step that may be added to the mechanical smoothing of the ferrous alloys to partly compensate for the deficiencies of the chemical etchants; namely, a final smoothing on one of the still finer powders. Washed rouge, alumina and magnesia are available. The latter, under the trade name of "Shamva," was used for the final rubbing of Fig. 23.

It should be explained that this last additional rubbing is done on the moist and heaped powder, as in the cases of the carborundum and tripoli. The specimen is not allowed to come in contact with the chamois skin that is stretched on the board. Also, the purpose is not to produce a burnished surface but merely to smooth preparatory to the chemical attack. The final elimination of scratches is left for the chemical etchant.

FIGS. 19 TO 24. (Captions on opposite page.)

This additional smoothing undoubtedly relieves the work of the etchant but was not used for preparing the surfaces for the photomicrographs of Figs. 21 to 36 except in the cases of Figs. 23 and 24. The latter shows a section through a low-carbon (0.10 per cent.) steel wire that was finished on Shamva and then slightly etched with nitric acid in alcohol. This print shows the pearlitic areas already dissolving deeply before the grain boundaries are hardly more than indicated. The scratches begin to disappear as some of the grain surfaces become noticeably roughened.

A light etching makes the final rubbing on rouge or Shamva more effective, since these soft powders have very little tooth for a surface already rubbed. The partial etching allows some of the metal to become free, smudge the powder, and hasten the smoothing.

A surface of ingot iron that was lightly etched and repolished on tripoli before the final etching is shown in Fig. 25. The final etching was so light that the crystal boundaries are hardly more than hair lines yet the acid has cleared the scratches and left the globules of oxide sharply defined.

A specimen of 0.33 per cent. carbon wire is given in longitudinal section in Fig. 26. This is a portion of an ordinary 8 by 10-in. laboratory print made to show the nature of the wire, especially the condition of the pearlite, and indicates the extensive spheroidizing of the cementite during the annealing.

Chloric Acid an Etching Reagent

While searching for a more suitable etchant than the usual nitric acid in alcohol or picric acid in alcohol, it was surmised that chloric acid might be serviceable. A solution of this acid can be prepared quickly by acidifying a saturated solution of potassium chlorate with sulfuric acid; ½ ml. of acid in 100 ml. of saturated chlorate solution is an active etchant.

A sample of 0.38 per cent. carbon steel wire, especially annealed for cold-heading work, was etched with the reagent. Immersion for only a few seconds sufficed to uncover the structure as seen in Fig. 27.

The same reagent was tried on a 0.90 per cent. carbon die steel, with the results seen in Fig. 28. This steel is low in sulfur, phosphorus and

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FIG. 19.—ALPHA BRASS. ETCHED WITH CONC. $NH_4OH + H_2O_2$. × 100. SCLEROSCOPE HARDNESS = 19.

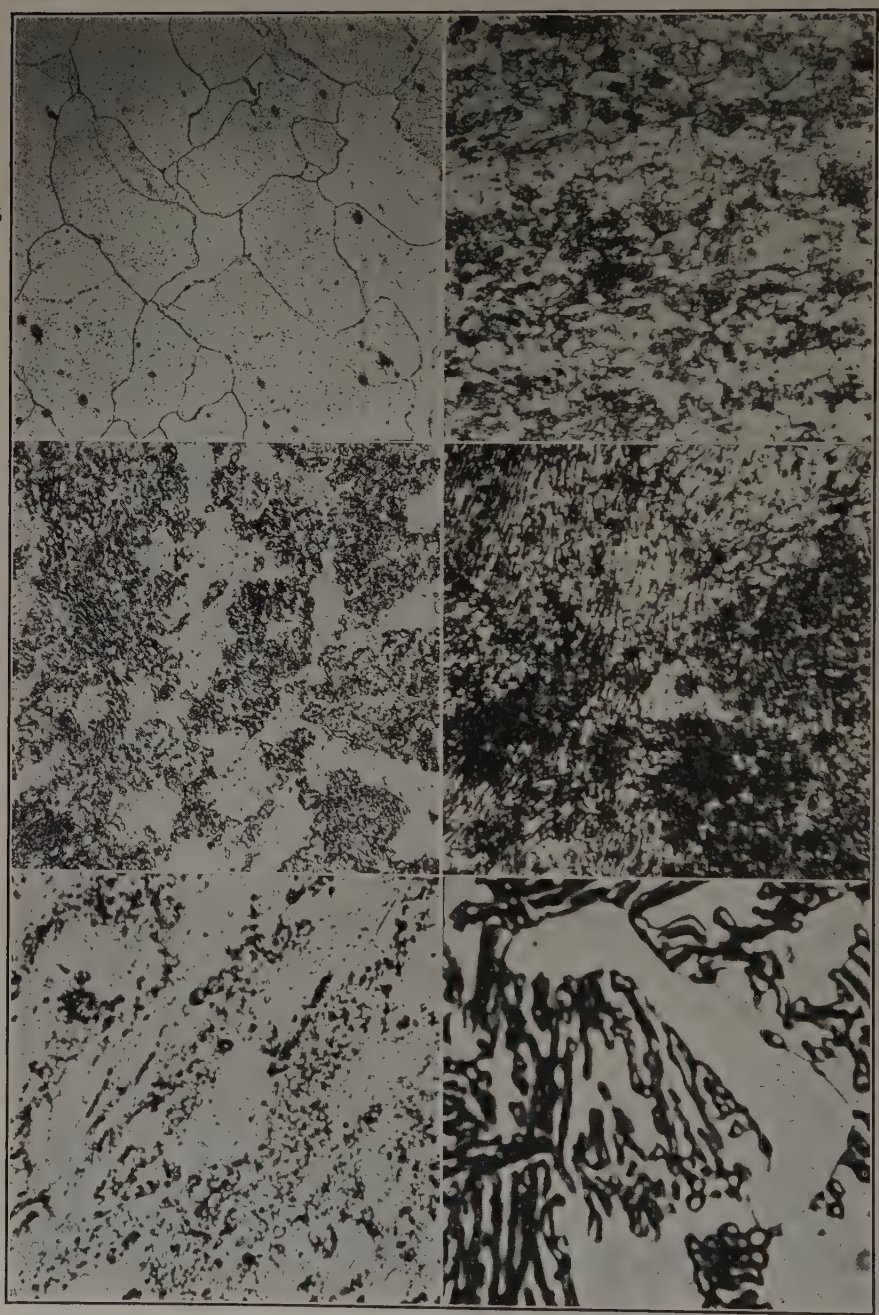
FIG. 20.—ALPHA BRASS. ETCHED WITH CONC. $HNO_3 + CrO_3$. × 100. SCLEROSCOPE HARDNESS = 14.

FIG. 21.—INGOT IRON. FINAL SMOOTHING ON HEAPED TRIPOLI. × 500.

FIG. 22.—INGOT IRON, SMOOTHED ON TRIPOLI. × 500. CRYSTALS OF ALUMINA IN GLOBULES OF OXIDE.

FIG. 23.—STEEL WIRE, 0.10 PER CENT. CARBON. FINAL SMOOTHING ON "SHAMVA." × 500.

FIG. 24.—STEEL WIRE, 0.10 PER CENT. CARBON. FINISHED ON SHAMVA AND ETCHED 1 MIN. IN 0.5 PER CENT. HNO_3 IN ALCOHOL. × 500.



FIGS. 25 TO 30. (Captions on opposite page.)

manganese. Its Brinell hardness is 160. Some portions of the print appear hazy; this is caused by waviness of the surface rather than by the presence of "unresolvable" aggregate. Proper focusing brings all spots to show sharply ordered pearlite. The depth of the chemical attack evidently depends on the orientation of the lamellas.

Preliminary tests indicate that this etchant is not suitable for deeper or longer etching. Promiscuous corrosion starts from numerous centers much worse than with nitric or picric acids in alcohol.

Comparison of High and Low Magnifications

It is interesting to find that specimens prepared without the use of wheels appear to as good advantage at high as well as low powers of magnification. Another print at 1500 dia. is given in Fig. 29. This is one of the newer high-manganese, high-sulfur open-hearth steels as annealed for cold-heading operations. The cementite in the pearlite seems to be largely in globules and the ferritic areas are relatively large for a 0.25 per cent. carbon steel.

The same 0.33 per cent. carbon wire shown in Fig. 26 at 200 dia. is given again in Fig. 30 at 3000 dia. The coarse pearlite and the numerous spherulites of cementite appear prominently and clearly at this magnification. Another wire, of the same carbon content, is shown in Fig. 31 at 3000 dia. This is a normalized material and is 50 points harder on the Brinell scale. Each material has its special suitability in cold-heading work.

Unusual Structure in Low-carbon Steels

During the search for etching reagents most suitable for steel, an unusual structure was discovered in certain low-carbon (0.12 per cent.) products.

The particular pieces in question had been quenched from 1500° F. and gave a brittle, crystalline fracture. Most of the stock was unquestionably ferrite but the nature of the earlier pearlitic nodules between the grains was not at first clear.

FIG. 25.—INGOT IRON, REPOLISHED ON TRIPOLI. ETCHED 2 MIN. IN 0.5 PER CENT. HNO_3 IN ALCOHOL. × 100.

FIG. 26.—ANNEALED STEEL WIRE, 0.33 PER CENT. CARBON. ETCHED WITH PICRIC ACID IN ALCOHOL. × 200. BRINELL HARDNESS = 120.

FIG. 27.—ANNEALED STEEL WIRE, 0.38 PER CENT. CARBON. ETCHED 10 SEC. IN SATURATED $KClO_3$ + 0.5 PER CENT. H_2SO_4. × 500. WIRE 0.600 IN. DIA., BRINELL HARDNESS = 163.

FIG. 28.—DIE STEEL, 0.90 PER CENT. CARBON. ETCHED 2 SEC. IN SATURATED $KClO_3$ + 0.5 PER CENT. H_2SO_4. × 1500. BRINELL HARDNESS = 160.

FIG. 29.—STEEL WIRE, 0.368 IN. DIA. FINISHED ON ROUGE. ETCHED 1.3 MIN. IN SATURATED PICRIC ACID IN ALCOHOL. LONGITUDINAL, × 1500. SCLEROSCOPE HARDNESS = 20.

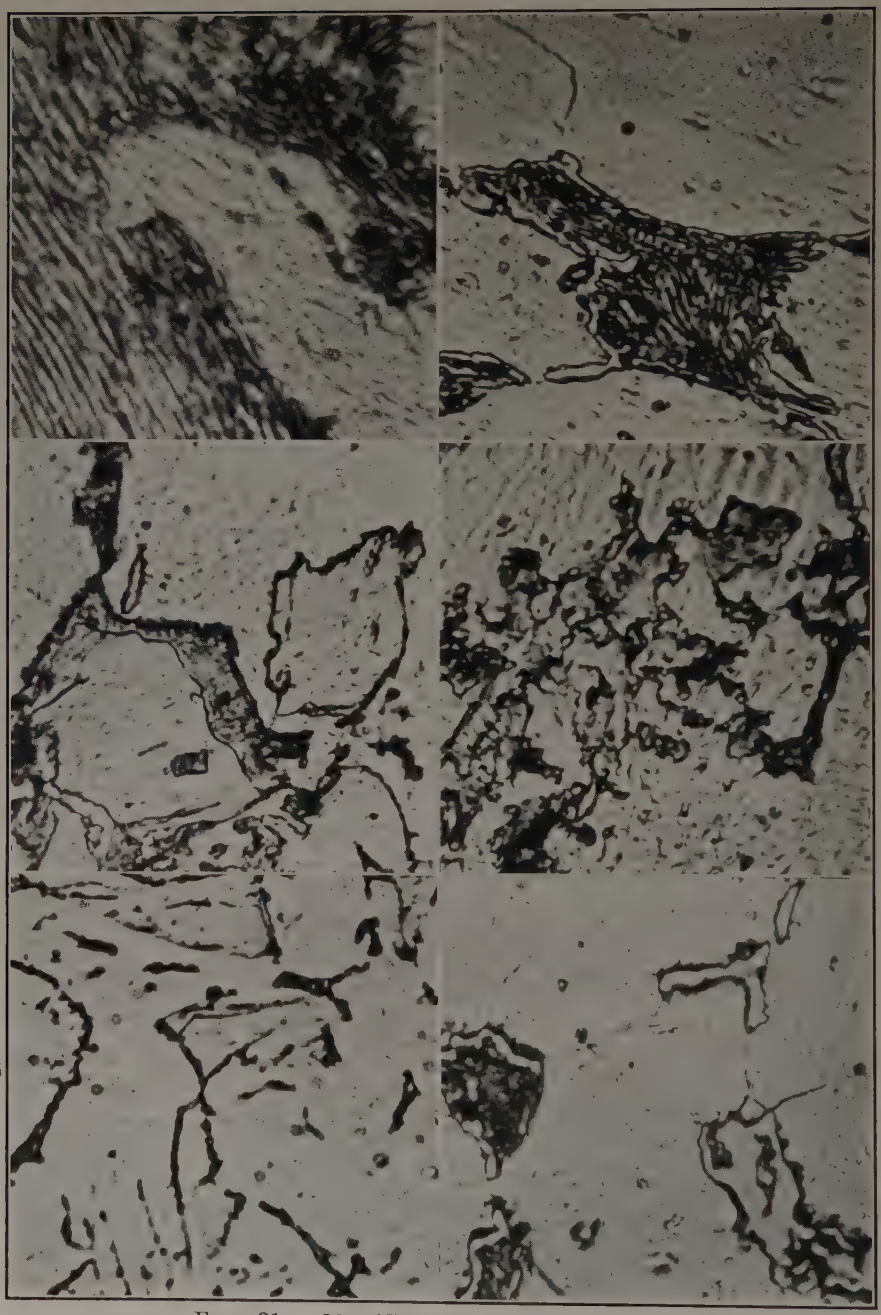
Carbon, 0.25 per cent. Manganese, 1.60 per cent. Sulfur, 0.09 per cent.

FIG. 30.—STEEL WIRE, 0.33 PER CENT. CARBON. POT ANNEALED. ETCHED WITH PICRIC ACID IN ALCOHOL. LONGITUDINAL, × 3000. BRINELL HARDNESS = 120.

31 32

33 34

35 36



FIGS. 31 TO 36. (Captions on opposite page.)

When some of the sections were etched lightly with hydrochloric acid in alcohol and examined at 2000 dia. magnification, the real condition was disclosed. The heating and quenching had transformed the original pearlitic nodules into martensite and troostite. The carbon in the pearlite had failed to disseminate throughout the ferrite and, in a miniature way, had formed the constituents of high-carbon quenched steel in a low-carbon matrix.

A typical nodule of pearlite as found in the original 0.12 per cent. carbon wire is shown in Fig. 32. This amount of carbon may be calculated to give about 14 per cent. of pearlite, the 86 per cent. remaining being ferrite.

One of the quenched structures is shown in Fig. 33. The central area surrounded by the dark fringe etches in an entirely different manner from the surrounding ferrite. The dark fringe dissolves very easily and is evidently troostite or merging into sorbite.

The dark fringes dissolve quickly in nitric or picric acid in alcohol so that in an ordinary etching to bring out the ferrite grains their nature is lost. However, later careful etching with the latter reagents gave the same results as the discovery etch with hydrochloric acid in alcohol.

Cap screws with the hardened nodules may have a tensile strength of 120,000 lb. per sq. in. The original pearlitic wire has about 65,000 lb. per sq. in. tensile strength.

Certain pieces from the same heats contained nodules lacking the central martensitic cores. Their strength was under 100,000 lb. per sq. in. and their fracture fibrous. The fringe component is present interspersed with ferrite. One of these nodules is shown in Fig. 34.

When steel of this same carbon content is heated to 1650° F. and quenched, the carbon is found to have been uniformly dispersed and to separate in a form resembling troostite, but in thin plates and in definite patterns. The patterns probably follow certain crystal planes of the transient gamma ferrite solid solution.

This condition is shown in Fig. 35. This sort of structure gives cap screws that have a fibrous fracture, excellent elongation and tensile

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Fig. 31.—Steel wire, 0.33 per cent. carbon, normalized. Etched with picric acid in alcohol. Longitudinal, × 3000. Brinell hardness = 170.

Fig. 32.—Pearlite in 0.12 per cent. carbon steel. Etched with picric acid in alcohol. × 2000. Brinell hardness = 120.

Fig. 33.—Nodule in quenched 0.12 per cent. carbon steel. Etched with HCl in alcohol. × 2000. Crystal of martensite (center) surrounded by troostite (dark). Brinell hardness = 170.

Fig. 34.—Nodule in quenched 0.12 per cent. carbon steel. Mixture of troostite and ferrite. Etched with picric acid in alcohol. × 2000. Brinell hardness = 150.

Fig. 35.—Quenched 0.12 per cent. carbon steel. Heated to 1650° F. before quenching. Etched with picric acid in alcohol. × 2000. Troostite dispersed in ferrite. Brinell hardness = 130.

Fig. 36.—Steel containing 0.12 per cent. carbon. Quenched from 1500° F., then annealed. Etched with picric acid in alcohol. × 2000. Cementite largely coalesced.

strength of about 90,000 lb. per sq. in. Quenching from yet higher temperatures develops the low-carbon martensites described by Dr. Jeffries.[3]

Behavior of Martensitic Nodules on Annealing

A final observation relates to the behavior of the martensitic nodules on annealing. They tend to revert to massive cementite instead of to pearlite. Frequently the cementite is found entirely massive and simply embedded in the ferrite. Sometimes the pearlite persists merely as a core surrounded by a shell of cementite.

Fig. 36 has been selected to show both conditions. Some of the cementite is massive, some shows slight dispersion, and some spots have rims of cementite about a pearlitic core. The massive cementite always occupies a space strikingly smaller than the original pearlitic nodule.

The discovery of this specific cause for the brittleness of quenched low-carbon steel has considerable significance for plants treating this sort of steel. The cause for a very disagreeable property in the steel is plain and steps can be taken to prevent its occurrence.

With the usual etching and low magnification these quenched structures are easily passed off for pearlite. The more delicate etching with hydrochloric acid in alcohol and the higher magnification instantly disclosed the actual condition.

The photomicrographs of Figs. 25 to 36 are from specimens prepared in the rapid way with the final smoothing on tripoli.

DISCUSSION

F. H. Clark, New York, N. Y.—I would like to ask the author what kind of tripoli powder he uses and to what extent, if any, these beryllium-copper alloys are being used commercially.

H. B. Pulsifer.—I have found it essential to use the finest abrasive that can be procured and to give it additional washing in the laboratory. The sharp cutting qualities of the carborundum powder add greatly to the effectiveness of the hand method of smoothing. This powder is the finest grade made by the Carborundum Co. and is further suspended and washed until it produces no large scratches on the specimens.

The same method of preparation applies to the tripoli powder. No particular brand is used. The ground tripoli obtained in bulk is simply given six successive one-minute suspensions in water and settled for use. The material prepared in this way will not give any coarse scratches when used damp and heaped on chamois skin.

As regards the use of the beryllium alloys, only the announcements have been made that the addition of beryllium to nickel and copper alloys makes the most striking change in properties. Although the Brinell hardness may be extremely high, it is not known that any commercial uses have yet been made of the alloys.

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[3] Zay Jeffries: A Contribution to the Theory of Hardening and the Constitution of Steel. *Trans.* Amer. Soc. Steel Treat. (1928) **13,** 369.

Treatment and Structure of Magnesium Alloys

By John A. Gann,* Midland, Mich.

(Philadelphia Meeting, October, 1928)

The following investigation constitutes a brief résumé of the more important binary magnesium alloys from the standpoint of metallographic technique, and the effect of heat treatment on structure and properties. The comparative newness of the subject justifies this procedure as a preface to a more detailed study of each individual series of alloys.

The work was started with the idea of practical application in the industry rather than as a theoretical investigation. The alloy compositions studied were selected as those most likely to show whether heat treatment would produce beneficial results. Furthermore, it was considered satisfactory to use commercial 99.9 per cent. magnesium, the best commercial grade of alloying ingredients, and to limit the time of heat treatment at the expense of incomplete equilibrium. These facts must be kept in mind when examining the results obtained, and the conclusions drawn.

Preparation of Alloys

All melts were made in an oil-fired cast-steel pot, approximately 12 in. dia. by 12 in. deep. Approximately 15 lb. of flux and 50 lb. of magnesium were melted and the calculated amount of alloying metal was added. After thorough alloying and puddling, the metal was chill cast in a graphite mold with four ½ by ½ by 4 in. bars fed from a common sprue and runner. The next higher composition alloy in a given series was made by adding the calculated amount of metal to the heel from the preceding cast. The pot was thoroughly cleaned after each series and new flux then introduced, thus avoiding possible contamination from earlier melts. The percentage compositions given in Table 1 are the calculated values. While not all alloys were analyzed, enough were checked to indicate that the reported compositions are correct to a few tenths of one per cent. A more detailed description of the foundry methods employed has been given in a previous paper.[1]

* Metallurgist, The Dow Chemical Co.

[1] J. A. Gann and A. W. Winston: Magnesium and Its Alloys. *Ind. & Eng. Chem.* (1927) **19**, 1193.

TABLE 1.—*Specimen Record and Heat-treating Schedule*

Composition	Number*	Solution Heat Treatment, Temperature ° C.		
		A	*B*	*C*
Mg (Commercial)	4385	500	510	520
Mg-4 Cd	4392	450	460	470
Mg-8 Cd	4393	450	460	470
Mg-12 Cd	4394	450	460	470
Mg-4 Al	4386	390	400	410
Mg-6 Al	4387	390	400	410
Mg-8 Al	4388	390	400	410
Mg-10 Al	4389	390	400	410
Mg-13 Al	4390	390	400	410
Mg-6 Al	4351	Sand cast		
Mg-8 Al	185–5	Sand cast—Sol. H. T. 2 hr. at 800° C., Furnace cooled.		
Mg-1 Zn	4428	300	310	320
Mg-2 Zn	4429	300	310	320
Mg-4 Zn	4430	300	310	320
Mg-6 Zn	4431	300	310	320
Mg-8 Zn	4432	300	310	320
Mg-1 Sn	4413	450	460	470
Mg-2 Sn	4414	450	460	470
Mg-4 Sn	4415	450	460	470
Mg-6 Sn	4416	450	460	470
Mg-8 Sn	4417	450	460	470
Mg-0.1 Mn	4409	500	510	520
Mg-0.2 Mn	4410	500	510	520
Mg-0.4 Mn	4411	500	510	520
Mg-1.0 Mn	4412	500	510	520
Mg-0.25 Cu	4397	420	430	440
Mg-0.50 Cu	4398	420	430	440
Mg-1 Cu	4399	420	430	440
Mg-2 Cu	4400	420	430	440
Mg-4 Cu	4401	420	430	440
Mg-8 Cu	4402	420	430	440
Mg-0.25 Ni	4403	440	450	460
Mg-0.50 Ni	4404	440	450	460
Mg-1 Ni	4405	440	450	460
Mg-2 Ni	4406	440	450	460
Mg-4 Ni	4407	440	450	460
Mg-8 Ni	4408	440	450	460

* Specimen numbers without dash numbers refer to the cast condition.

−30 12 hr. at temp. A + 12 hr. at B + 12 hr. at C—quenched in water.
−31 Solution treatment as for −30, plus 8 hr. at 150° C.
−32 Solution treatment as for −30, plus 24 hr. at 150° C.
−33 Solution treatment as for −30, plus 72 hr. at 150° C.
−35 Solution treatment as for −30, plus 8 hr. at 250° C.
−36 Solution treatment as for −30, plus 24 hr. at 250° C.
−37 Solution treatment as for −30, plus 72 hr. at 250° C.
−37a Treatment as for −37 plus 24 hr. at 300° C.

Heat Treatment

All alloy compositions investigated were submitted to a solution heat treatment and to a solution plus precipitation heat treatment. These operations were conducted in an automatically controlled electric furnace. The solution-heat-treated specimens were quenched in cold water, while air cooling was considered satisfactory after the precipitation heat treatment. Because of the slight oxidation that occurred on certain alloys, all specimens had 1/16 in. of metal machined off the faces used for structural and hardness investigations.

Specimens were solution-heat-treated for 12, 24, and 36 hr. at the temperatures given in Table 1. In many instances it was not feasible to heat-treat the alloy at a temperature close to the eutectic melting point. This was particularly true with alloys having high-melting eutectics. Many magnesium alloys are characterized by the fact that they will withstand a given temperature for a moderate time, but oxidize badly if held at this same temperature for a much longer period. The temperatures used were chosen after a preliminary survey to determine the safe upper limits for prolonged heating. Maximum changes in structure and properties were obtained in samples subjected to 36-hr. solution heat treatment, although in some of the compositions of lower percentage this optimum effect was reached in a somewhat shorter time.

Precipitation or aging treatments at 150° and 250° C. for 8, 24, and 72 hr. were given after each of the above solution heat treatments. Where this aging was effective, maximum hardnesses were obtained on specimens that had been given the longer solution heat treatment. For the sake of brevity, the only results here given are on specimens solution-heat-treated 36 hr., followed by the various precipitation heat treatments.

Hardness Determinations

The hardness test was selected as the most satisfactory method of indicating changes in properties, especially those due to precipitation heat treatment. The Brinell hardness determination on magnesium alloys is not as accurate as desired, on account of the coarse grain structure and the elliptical or irregular impressions sometimes produced. This is particularly true in the softer alloys and those of lower percentage composition. Much greater accuracy is here obtained with the Rockwell machine. These facts, coupled with the relative speeds of making determinations by these two methods, seemed to justify the use of the Rockwell test in this work, even though it thereby precluded a direct comparison with most of the existing hardness data on magnesium alloys. This problem was finally settled after it had been established that a definite relationship existed between the results obtained by the

TABLE 2.—*Rockwell "E" Hardness Determinations*

Composition	Treatment							
	Cast	−30	−31	−32	−33	−35	−36	−37
Mg (Commercial)	11	20	17	19	20	18	17	15
Mg-4 Cd	20	28	24	30	25	28	26	23
Mg-8 Cd	25	30	30	31	28	29	31	26
Mg-12 Cd	35	35	35	38	38	35	35	33
Mg-4 Al	42	39	39	41	40	39	38	39
Mg-6 Al	51	48	49	51	51	50	50	50
Mg-8 Al	62	61	62	72	82	77	77	73
Mg-10 Al	74	65	75	92	92	84	84	82
Mg-13 Al	80	78	87	98	99	90	91	88
Mg-1 Zn	19	29	30	30	31	28	27	24
Mg-2 Zn	29	32	38	39	40	31	30	30
Mg-4 Zn	43	41	50	64	68	42	45	43
Mg-6 Zn	54	50	68	82	81	60	59	57
Mg-8 Zn	57	55	80	82	84	63	63	59
Mg-1 Sn	17	27	23	20	20	18	13	10
Mg-2 Sn	19	20	25	24	23	22	19	21
Mg-4 Sn	25	26	26	27	27	23	27	30
Mg-6 Sn	32	36	36	32	32	34	37	39
Mg-8 Sn	41	39	40	38	35	37	40	50
Mg-0.1 Mn	22	27	25	23	24	19	18	17
Mg-0.2 Mn	24	26	24	22	23	21	23	23
Mg-0.4 Mn	23	22	21	19	21	18	20	21
Mg-1 Mn	21	26	29	24	22	21	18	19
Mg-0.25 Cu	27	28	27	25	24	19	20	23
Mg-0.50 Cu	36	31	26	26	24	22	19	20
Mg-1 Cu	30	30	27	27	25	22	22	24
Mg-2 Cu	37	32	28	30	27	26	26	25
Mg-4 Cu	40	35	34	33	33	31	30	31
Mg-8 Cu	63	50	47	46	46	46	43	45
Mg-0.25 Ni	13	20	15	15	15	13	13	11
Mg-0.50 Ni	23	23	18	19	20	18	13	15
Mg-1 Ni	24	29	23	21	20	20	21	20
Mg-2 Ni	32	31	30	29	29	25	28	27
Mg-4 Ni	43	34	34	33	34	34	33	33
Mg-8 Ni	60	50	48	44	47	47	48	47

TABLE 3.—*Brinell Hardness*
Derived from Rockwell "E" Determinations

Composition	Treatment							
	Cast	−30	−31	−32	−33	−35	−36	−37
Mg (Commercial)	34.7	36.5	36.0	36.3	36.5	36.1	36.0	35.5
Mg-4 Cd	36.5	38.5	37.5	39.0	37.8	38.5	38.0	37.2
Mg-8 Cd	37.8	39.0	39.0	39.0	38.5	38.7	39.2	38.0
Mg-12 Cd	40.3	40.3	40.3	41.1	41.1	40.3	40.3	39.8
Mg-4 Al	42.5	41.5	41.5	42.2	41.8	41.5	41.1	41.5
Mg-6 Al	46.0	44.8	45.2	46.0	46.0	45.6	45.6	45.6
Mg-8 Al	51.8	51.0	51.8	60.5	72.6	66.2	66.2	61.5
Mg-10 Al	62.8	54.1	63.9	88.0	88.0	75.8	75.8	72.6
Mg-13 Al	70.0	67.4	80.0	99.0	100.8	85.0	86.5	81.8
Mg-1 Zn	36.3	38.7	39.0	39.0	39.2	38.5	38.2	37.5
Mg-2 Zn	38.7	39.5	41.1	41.5	41.8	39.2	39.0	39.0
Mg-4 Zn	42.8	42.2	45.6	53.3	56.7	42.5	43.5	42.8
Mg-6 Zn	47.3	45.6	56.7	72.6	71.3	50.5	49.9	48.9
Mg-8 Zn	48.9	47.9	70.0	72.6	75.8	52.5	52.5	49.9
Mg-1 Sn	36.0	38.2	37.2	36.5	36.5	36.1	35.0	34.5
Mg-2 Sn	36.3	36.5	37.8	37.5	37.2	37.0	36.3	36.8
Mg-4 Sn	37.8	38.0	38.0	38.2	38.2	37.2	38.2	39.0
Mg-6 Sn	39.5	40.5	40.5	39.5	39.5	40.0	40.8	41.5
Mg-8 Sn	42.2	41.5	41.8	41.1	40.3	40.8	41.8	45.6
Mg-0.1 Mn	37.0	38.2	37.8	37.2	37.5	36.3	36.1	36.0
Mg-0.2 Mn	37.5	38.0	37.5	37.0	37.2	36.8	37.2	37.2
Mg-0.4 Mn	37.2	37.0	36.8	36.3	36.8	36.1	36.5	36.8
Mg-1 Mn	36.8	38.0	38.7	37.5	37.0	36.8	36.1	36.3
Mg-0.25 Cu	38.2	38.5	38.2	37.8	37.5	36.3	36.5	37.2
Mg-0.50 Cu	40.5	39.2	38.0	38.0	37.5	37.0	36.3	36.5
Mg-1 Cu	39.0	39.0	38.2	38.2	37.8	37.0	37.0	37.5
Mg-2 Cu	40.8	39.5	38.5	39.0	38.2	38.0	38.0	37.8
Mg-4 Cu	41.8	40.3	40.0	39.8	39.8	39.2	39.0	39.2
Mg-8 Cu	52.5	45.6	44.3	44.0	44.0	44.0	42.8	43.5
Mg-0.25 Ni	35.0	36.5	35.5	35.5	35.5	35.0	35.0	34.7
Mg-0.50 Ni	37.2	37.2	36.1	36.3	36.5	36.1	35.0	35.5
Mg-1 Ni	37.5	38.7	37.2	36.8	36.5	36.5	36.8	36.5
Mg-2 Ni	39.5	39.2	39.0	38.7	38.7	37.8	38.5	38.2
Mg-4 Ni	42.8	40.0	40.0	39.8	40.0	40.0	39.8	39.8
Mg-8 Ni	50.5	45.6	44.8	43.1	44.3	44.3	44.8	44.3

two methods, and that the accuracy of the Brinell hardness values as derived from the Rockwell results were independent of the composition or heat treatment of the magnesium alloy.[2] The original Rockwell hardness data are given in Table 2, and the corresponding Brinell hardness values in Table 3.

Increasing the percentage of the added ingredient increases the hardness of the alloy in both the cast and heat-treated conditions. Solution heat treatment has little or no effect on the hardness of low-percentage alloys. The small changes here reported are probably due to a combination of factors, including variations in grain size and small structural changes similar to those described below. The most pronounced effects occur in the higher percentage aluminum, copper, and nickel alloys. The softening in the magnesium-aluminum series is due to the solution of the magnesium-aluminum eutectic, while in the magnesium-copper and magnesium-nickel series, it is due to a spheroidizing of these eutectics.

Age-hardening phenomena are observed in the higher percentage magnesium-aluminum, magnesium-zinc, and magnesium-tin alloys, where increases in Brinell hardness of 45, 55, and 8 per cent. respectively were obtained. Maximum hardness in the magnesium-aluminum and magnesium-zinc alloys occurred after 72 hr. at 150° C., although practically the same hardness was obtained after 24 hr. at the same temperature. Aging at 250° C. caused further growth or coalescence of the precipitated particles which lowered the hardness and affected the microstructure. The precipitation in the magnesium-tin alloys appeared to proceed more slowly, requiring a higher temperature and longer time.

Metallography

The grinding and polishing of specimens was carried out on rotating wheels as follows:

Cloth	Abrasive	Speed R.p.m.
Aloxite No. 1½		750
Aloxite No. 150		750
Canvas	XF Alundum	750
Velvet	XF Alundum	500
Velvet	600 Alundum	400
Velvet	Levigated Alumina	300 or 150

The alumina is suspended in 0.001 normal NaOH in order to reduce tarnishing. A dilute soap solution is added to the velvet wheels as needed, in order to prevent seizing of the specimens. It has been found desirable to rotate the specimens during polishing. The shorter the time on the alumina wheel the less is the relief polish and the sharper are the outlines of the compound particles. After rinsing off any adhering polishing compound, the specimen is transferred directly to the etchant

[2] Detailed data covering this relationship will be published later.

without drying (except in the case of nonaqueous etchants). The specimen is continuously shaken in the etchant, or gently swabbed with a tuft of cotton. In either case, the surface of the specimen should be completely immersed. After washing in running water the specimen is rinsed in acetone and dried in a blast of warm air.

The various structural details of magnesium alloys are developed to different degrees by each etching reagent. Table 4 gives a general résumé of the tendencies obtained by several operators. The conclusions stated here refer primarily to the cast alloys, since heat treatment may not only remove coring and dissolve a constituent, but may also change the detail in the groundmass and permit the development of sharp grain boundaries. In this work, groundmass detail includes coring effects, evidences of precipitation from solid solution, and the delineation of twins. The amount of alloying metal present is likewise important. In low percentage eutectic-forming alloys, the added metal often appears as individual, well defined, intermetallic compound crystals. No true eutectic structure is seen except in higher percentage alloys. The term "eutectic" in Table 4 refers to the form the added metal may take, such as compound, eutectic, or possibly elementary metal in the case of manganese.

Etching stains are very common in magnesium alloys, particularly those containing the heavy metals—cadmium, tin, and nickel. This phenomenon is due to a solution of such metal by the etchant, followed by contact plating on the magnesium-rich portions of the structure, and becomes more pronounced as the percentage of the added metal increases. In some cases the contact plate adheres firmly, but is so thin that it does not completely conceal the microstructure. In other instances it is so coarse and loosely held that its formation is largely prevented by swabbing with cotton or by etching in more concentrated acid where the violent gas evolution retards its formation.

Twins occur in large numbers in magnesium alloys. They are most abundant in low-percentage alloys, and are observed least often after solution heat treatment, and where compound precipitation and growth has proceeded far enough to affect the microstructure. This lack of visibility does not prove their absence. They are undoubtedly concealed by fine structural detail, the same as in commercially pure magnesium, where an etch that shows coring or dendritic segregation gives a poor delineation of twins.

Meissner, Hanson and Schmidt[3] have observed these twins in magnesium-zinc alloys subjected to precipitation heat treatment and Schmidt believes that "the parallel lines are twin lines caused by inner stresses due to the age-hardening effect, the mechanism of which has not yet been

[3] K. L. Meissner: Reply to discussion on Age-hardening Tests with Elektron Alloys. *Jnl.* Inst. Met. (1927) **38,** 216.

TABLE 4.—*Etching Behavior of Cast Magnesium Alloys*

	Etchant					
	2 Per Cent. HNO_3	2 Per Cent. HCl	1 Per Cent. H_2SO_4	2 Per Cent. $H_2C_2O_4$	2 Per Cent. HNO_3 (Alcoholic)	10 Per Cent. NH_4Cl
Alloy						
Magnesium						
Grain boundaries	Sharp	Sharp	Sharp	Sharp	Sharp	Sharp
Coring	Some	Some	Some	Some	None	None
Eutectic	None	None	None	None	None	None
Groundmass detail	Good	Good	Good	Good	Fair	Fair
Staining	None	None	None	None	None	None
Recommended	Yes	Yes	Yes	Yes	Yes	Yes
Magnesium-cadmium						
Grain boundaries	None	None	Faint	None	None	Faint[a]
Coring	Strong	Strong	Strong	Strong	Strong	Strong
Eutectic	None	None	None	None	None	None
Groundmass detail	None	None	Fair	None	None	Fair
Staining	Strong	Strong	Some	Strong	Strong	Some
Recommended	No	No	Yes	No	No	Yes
Magnesium-aluminum						
Grain boundaries	Some	Some	Some	Sharp	Some	None
Coring	Strong	Some	Some	Some	Some	Some
Eutectic	Good	Good	Good	Good	Good	Poor
Groundmass detail	Good	Poor	Poor	Fair	Good	Fair
Staining	None	None	None	None	None	None
Recommended	Yes	Yes	Yes	Yes	Yes	No
Magnesium-zinc						
Grain boundaries	Faint	None	None	None	Faint	None
Coring	Some	Some	Strong	Strong	Some	None
Eutectic	Good	Poor	Fair	Good	Good	Good
Groundmass detail	Fair	Poor	Fair	Fair	Fair	Poor
Staining	None	Strong	Some	Some	None	None
Recommended	Yes	No	No	No	Yes	No
Magnesium-tin						
Grain boundaries	None	None	None	Faint	None	None
Coring	Some	Some	Some	Some	Some	Some
Eutectic	Poor	Poor	Fair	Poor	Fair	Fair
Groundmass detail	None	None	None	Poor	None	None
Staining	Some	Some	Some	Some	Some	Some
Recommended	No	No	Yes	No	Yes	Yes
Magnesium-manganese						
Grain boundaries	Sharp	Sharp	Sharp	Sharp	Sharp	Sharp
Coring	Some	Some	Some	Strong	Some	Some
Eutectic	Good	Good	Good	Poor	Good	Good
Groundmass detail	Fair	Fair	Fair	Fair	Fair	Fair
Staining	None	None	None	None	None	None
Recommended	Yes	Yes	Yes	Yes	Yes	Yes
Magnesium-copper						
Grain boundaries	None	None	None	None	None	None
Coring	None	None	None	None	None	None
Eutectic	Good	Good	Good	Fair	Good	Poor
Groundmass detail	Fair	Fair	Fair	Fair	Fair	Poor
Staining	None	None	None	None	None	Strong
Recommended	Yes	Yes	Yes	Yes	Yes	No
Magnesium-nickel						
Grain boundaries	None	None	None	None	None	None
Coring	None	None	None	None	None	None
Eutectic	Good	Poor	Poor	Good	Good	Poor
Groundmass detail	Fair	Poor	Poor	Fair	Fair	Poor
Staining	None	Strong	Strong	None	Some	Strong
Recommended	Yes	No	No	Yes	No	No

[a] 10 per cent. NH_4NO_3.
[b] 2 per cent. alcoholic HCl.

fully explained." We agree that alloys thus treated contain many twins, but cannot accept their view as to the cause. In the first place, these twins occur in magnesium alloys that do not age-harden, and are most

abundant in pure magnesium. Again, annealing at age-hardening temperatures instead of producing strains should relieve those already existing. A satisfactory explanation for this phenomenon is to consider that this structure is due to annealing twins. The quenching operation following solution heat treatment subjects the metal to sufficient strain to cause their formation when the metal is subsequently heated. It is true, these twins are often produced without this heating step. It appears probable that an exceedingly small amount of strain followed or accompanied by an exceedingly small amount of heating is sufficient for their development.

Magnesium

The structure of magnesium has been discussed in considerable detail by Pulsifer[4] and by the author[5] in his discussion of Pulsifer's paper.

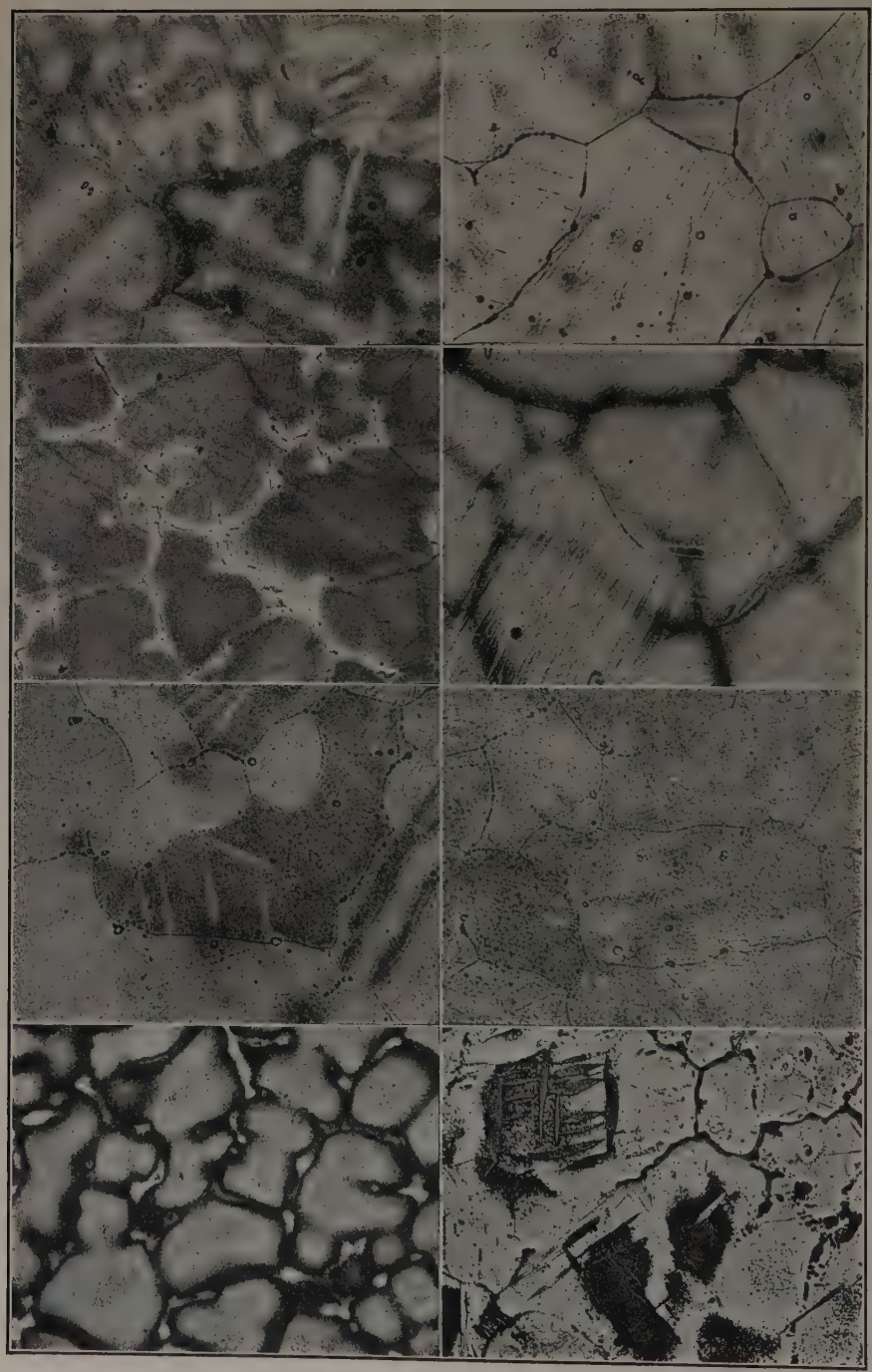
Fig. 1.—Magnesium No. 4385. × 200. Chill cast. Etched 10 per cent. NH_4NO_3.

Inasmuch as the pure metal is not susceptible to heat treatment, it has been considered satisfactory for our present purpose to reproduce but one photograph of pure magnesium.

Fig. 1 shows a sample of chill-cast magnesium etched 45 sec. in 10 per cent. ammonium nitrate. It shows all the structural features occurring in pure magnesium, with the exception of dendritic coring as developed by long etchings in ammonium salts, or a short-time etch in dilute

[4] H. B. Pulsifer: Magnesium—Its Etching and Structure. *Proc.* Inst. Met. Div. (1928) 461.

[5] J. A. Gann: Discussion of paper by H. B. Pulsifer. *Idem.*, 477.



FIGS. 2–9.—(Captions on opposite page.)

acid. This particular field was selected largely because of the twins present. We have occasionally observed what appeared to be a single twin jumping across a crystal boundary, but it was thought that this phenomenon might be due to an accidental arrangement of two twins in adjacent crystals. In this particular instance, however, three well defined parallel twins cross a given crystal boundary. The largest one

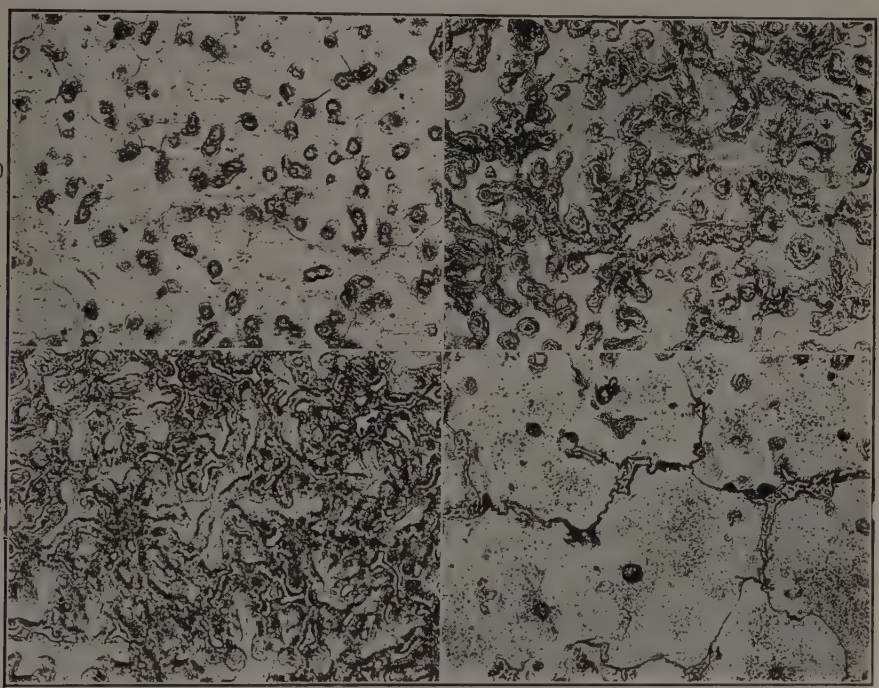
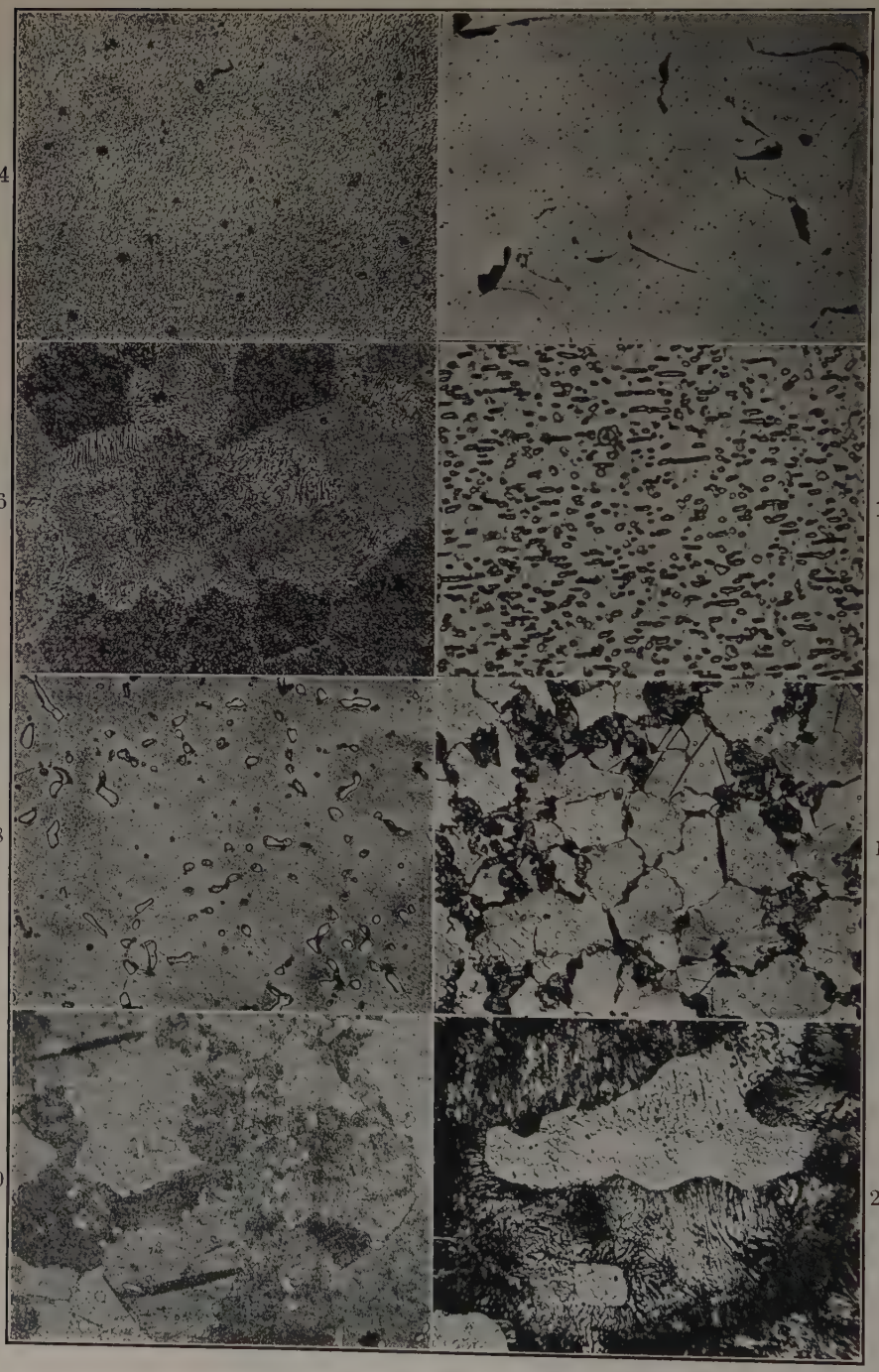


FIG. 10.—MG-4 AL, No. 4386. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 11.—MG-8 AL, No. 4388. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 12.—MG-13 AL, No. 4390. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 13.—MG-6 AL, No. 4351. ×200. SAND CAST. ETCHED 2 PER CENT. $H_2C_2O_4$.

shown in the photograph likewise crosses two crystal boundaries and appears to terminate in an isolated portion of the crystal containing most of this twin.

FIG. 2.—MG-4 CD, No. 4392. × 200. CHILL CAST. ETCHED 2 PER CENT. H_2SO_4.
FIG. 3.—MG-8 CD, No. 4393. × 200. CHILL CAST. ETCHED 2 PER CENT. H_2SO_4.
FIG. 4.—MG-12 CD, No. 4394. × 200. CHILL CAST. ETCHED 2 PER CENT. H_2SO_4.
FIG. 5.—MG-4 CD, No. 4392. × 200. CHILL CAST. ETCHED 10 PER CENT. NH_4NO_3.
FIG. 6.—MG-12 CD, No. 4394–30. × 200. SOLUTION HEAT TREATMENT. ETCHED 2 PER CENT. H_2SO_4.
FIG. 7.—MG-12 CD, No. 4394–32. × 200. PRECIPITATED AT 150° C. ETCHED 2 PER CENT. H_2SO_4.
FIG. 8.—MG-12 CD, No. 4394. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 9.—MG-12 CD, No. 4394. × 200. CHILL CAST. ETCHED 25 PER CENT. HNO_3.



FIGS. 14–21.—(Captions on opposite page.)

Magnesium-cadmium Alloys

The structures of the 4, 8 and 12 per cent. cast cadmium alloys, etched with 2 per cent. sulfuric acid, are reproduced in Figs. 2, 3, and 4. Within the range investigated these alloys form a complete series of solid solutions, and are characterized by pronounced coring and staining. The small amounts of impurities are exaggerated by the staining effects. Ammonium nitrate does not stain as much as most acids, and therefore better reveals the grain boundaries and twins (Fig. 5).

The solution heat treatment removes coring in all compositions examined. Twins are indistinctly seen through the stain film in the precipitation-heat-treated 12 per cent. alloy (Fig. 7), but are well defined in the corresponding solution heat-treated alloy (Fig. 6).

Fig. 8 represents the 12 per cent. cadmium alloy etched with 2 per cent. nitric acid. In some of the adjacent fields, this structure was approximately reversed on account of excessive staining, with the result that the center of the cored crystal was dark, and the periphery light. A tendency toward this staining reversal is shown in Figs. 4 and 8. Fig. 9 shows the same 12 per cent. cadmium alloy etched in 25 per cent. nitric acid. While there is still considerable staining, the action of the acid was sufficiently violent to prevent a continuous adhering film, with the result that the true structure of the alloy is more accurately portrayed than with the more dilute acid.

Magnesium-aluminum Alloys

The magnesium-aluminum alloys constitute the most important binary magnesium series, and as a result have been the subject of numerous investigations. Hanson and Gaylor[6] determined the constitutional diagram for the entire series. The solid solubility of aluminum in magnesium has been more accurately studied by Schmidt,[7] who con-

[6] D. Hanson and L. V. Gayler: The Constitution of the Alloys of Aluminum and Magnesium. *Jnt.* Inst. Met. (1920) **24**, 201.

[7] W. Schmidt: Beitrag zur Kenntnis der hochprozentigen Magnesiumlegierungen. *Ztsch. f. Metallkunde* (1927) **19**, 452.

Fig. 14.—Mg-8 Al, No. 4388–30. × 200. Solution heat treatment. Etched 5 per cent. HNO_3.

Fig. 15.—Mg-8 Al, No. 4388–32. × 200. Precipitated at 150° C. Etched 0.5 per cent. HNO_3.

Fig. 16.—Mg-8 Al, No. 4388–36. × 200. Precipitated at 250° C. Etched 0.5 per cent. HNO_3.

Fig. 17.—Mg-8 Al, No. 4388–37A. × 1000. Precipitated at 300° C. Etched 0.5 per cent. HNO_3.

Fig. 18.—Mg-13 Al, No. 4390–30. × 200. Solution heat treatment. Etched 5 per cent. HNO_3.

Fig. 19.—Mg-13 Al, No. 4390–32. × 200. Precipitated at 150° C. Etched 0.5 per cent. HNO_3.

Fig. 20.—Mg-13 Al, No. 4390–36. × 200. Precipitated at 250° C. Etched 0.5 per cent. HNO_3.

Fig. 21.—Mg-8 Al, No. 185–5. × 200. Solution heat treatment, furnace-cooled. Etched 2 per cent. HNO_3.

FIGS. 22–29.—(Captions on opposite page.)

cludes that the limits are 11 per cent. at the eutectic temperature 436° C., and about 7.5 per cent. at room temperature. Property changes due to heat treatment have been reported by Stoughton and Miyake,[8] and Meissner.[9] The microstructural changes due to heat treatment have been studied by numerous investigators, particularly by Schmidt. In general, our data confirm the work of the above observers both as to structure and hardness.

The microstructures of chill-cast alloys containing 4, 8, and 13 per cent. aluminum are shown in Figs. 10 to 12, inclusive. Nitric acid etching reveals the coring surrounding the Al_2Mg_3 compound particles. Most of these particles are so small that they do not stand out clearly except in the 13 per cent. alloy. In many respects, this is the most satisfactory etch for these alloys. Oxalic acid has the advantage over nitric acid in that it more often reveals the grain boundaries, but at the expense of coring (Fig. 13). This photograph shows that under certain cooling conditions a true eutectic structure may be formed in place of the individual compound crystals of Fig. 12.

The structural changes due to the heat treatment of the 8 per cent. alloy are shown in Figs. 14 to 17 and Fig. 21. Solution heat treatment gives the solid-solution structure shown in Fig. 14. Aging at 150° C. causes a precipitation of the Al_2Mg_3 compound in those areas richest in aluminum, which are indicated by the dark sections in Fig. 15. These dark areas have a sorbitic appearance with a tendency toward a lamellar pearlitic structure. The apparent clearing up of the groundmass in Fig. 15 is due to a lighter etch. The solution-heat-treated specimen of Fig. 14 was etched in 5 per cent. nitric acid, while the specimens in Figs. 15 to 17 were etched in 0.5 per cent. nitric acid. Annealing at a higher temperature, 250° C., appears to cause precipitation throughout most of the specimen, giving the pearlitic structure shown in Fig. 16. Annealing at 300° C. causes additional coalescence, and results in the structure

[8] B. Stoughton and M. Miyake: Preliminary Study of Magnesium-base Alloys. *Trans.* (1926) **73,** 541.

[9] K. L. Meissner: Age-hardening Tests with Electron Alloys. *Jnl.* Inst. Met. (1927) **38,** 195.

FIG. 22.—MG-4 ZN, No. 4430. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 23.—MG-6 ZN, No. 4431. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 24.—MG-8 ZN, No. 4432. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.
FIG. 25.—MG-4 ZN, No. 4430–36. × 200. PRECIPITATED AT 250° C. ETCHED 2 PER CENT. HNO_3.
FIG. 26.—MG-6 ZN, No. 4431–30. × 200. SOLUTION HEAT TREATMENT. ETCHED 2 PER CENT. HNO_3.
FIG. 27.—MG-6 ZN, No. 4431–32. × 200. PRECIPITATED AT 150° C. ETCHED 2 PER CENT. HNO_3.
FIG. 28.—MG-6 ZN, No. 4431–36. × 200. PRECIPITATED AT 250° C. ETCHED 2 PER CENT. HNO_3.
FIG. 29.—MG-6 ZN, No. 4431–37A. × 200. PRECIPITATED AT 300° C. ETCHED 2 PER CENT. HNO_3.

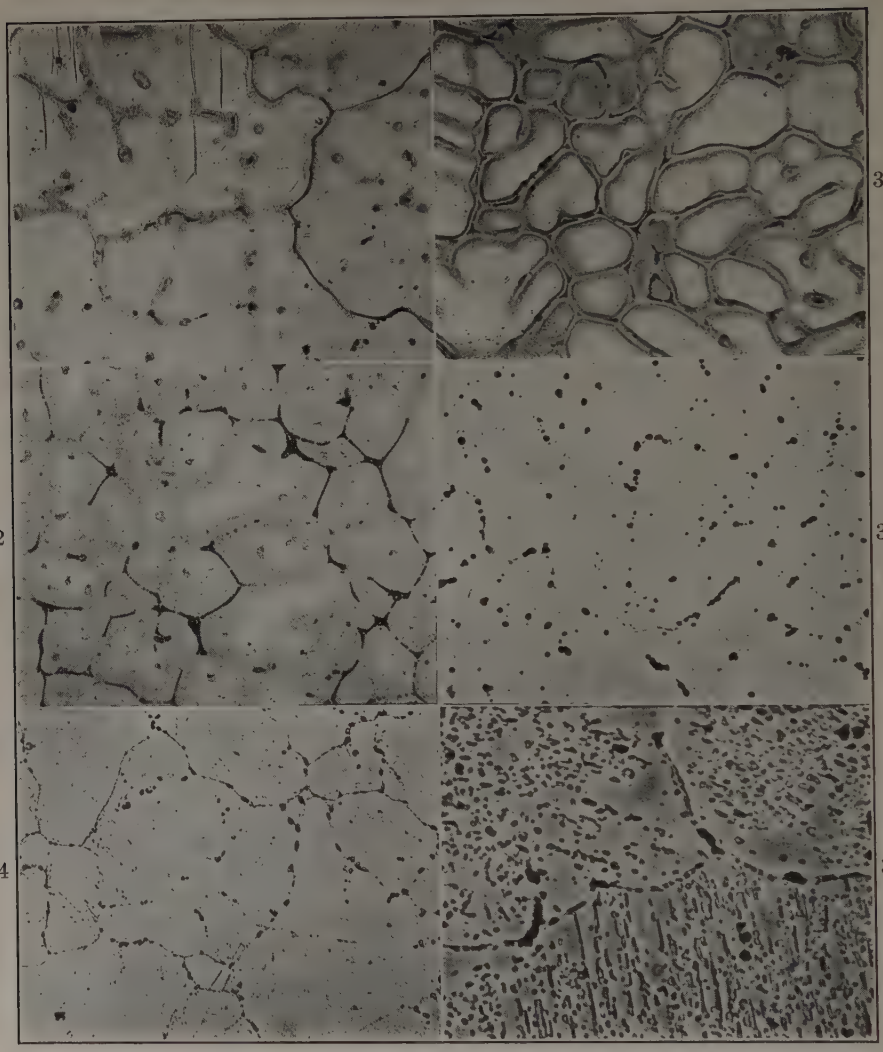


FIG. 30.—MG-1 SN, No. 4413. × 200. CHILL CAST. ETCHED 2 PER CENT. ALC. HNO_3.

FIG. 31.—MG-4 SN, No. 4415. × 200. CHILL CAST. ETCHED 2 PER CENT. ALC. HNO_3.

FIG. 32.—MG-8 SN, No. 4417. × 200. CHILL CAST. ETCHED 2 PER CENT. ALC. HNO_3.

FIG. 33.—MG-8 SN, No. 4417–30. × 200. SOLUTION HEAT TREATMENT. ETCHED 2 PER CENT. ALC. HNO_3.

FIG. 34.—MG-8 SN, No. 4417–32. × 200. PRECIPITATED AT 150° C. ETCHED 2 PER CENT. ALC. HNO_3.

FIG. 35.—MG-8 SN, No. 4417–37. × 200. PRECIPITATED AT 250° C. ETCHED 2 PER CENT. ALC. HNO_3.

shown in Fig. 17. Considerable precipitation takes place when a solution-heat-treated specimen is slowly cooled. Fig. 21 shows a furnace-cooled 8 per cent. alloy where the precipitated areas contain both the sorbitic and pearlitic type of structures merging into each other. Heat treatment of the 13 per cent. aluminum alloy gives results corresponding to those of the 8 per cent., except for the presence of excess massive Al_2Mg_3 crystals. This is indicated by Figs. 18 to 20, showing solution heat treatment and precipitation at 150° and 250° C. respectively.

Magnesium-zinc Alloys

It has been known for some time that magnesium-zinc alloys are susceptible to heat treatment, but there is difference of opinion as to the composition limits thus affected. Stoughton and Miyake[10] have stated that zinc up to 10 per cent. will form a solid solution with magnesium, and that the higher compositions may be age-hardened. Both their microstructures and hardness values are in good agreement with our findings. Chadwick[11] has studied the entire series of magnesium-zinc alloys. He concludes from his limited data that approximately 12.5 per cent. (5 atomic per cent.) zinc is soluble at 342° C., the eutectic temperature, and 3 per cent. (approximately 1 atomic per cent.) zinc is soluble at 250° C. A more detailed investigation of the solid solubility of zinc in magnesium has been made by Schmidt,[12] who found the solubility of zinc to be 6 per cent. at the eutectic temperature, and 2 per cent. at room temperature. Meissner[13] obtained age-hardening effects in alloys containing more than 2 per cent. zinc.

The structures of chill-cast alloys containing 4, 6, and 8 per cent. zinc are shown in Figs. 22 to 24. The outstanding structural features are the cored solid-solution crystals, and the increasing amounts of $Mg\text{-}Zn_2$ compound. Solution heat treatment removes coring and dissolves compound. The structure of the 6 per cent. solution-heat-treated alloy is shown in Fig. 26. Aging of the alloys at 150° C. produces no additional structural change except to help develop annealing twins (Fig. 27). Aging the 6 per cent. alloy at 250° C. resulted in sufficient growth of the precipitated $Mg\text{-}Zn_2$ particles to cause a distinct change in the structure (Fig. 28). Heating at 300° C. caused the groundmass to substantially clear up, due to the re-solution of the precipitated compound (Fig. 29). Aging the 4 per cent. alloy (Fig. 25) at 250° C., developed but little of the precipitated structure shown in Fig. 28, thus indicating that approximately 4 per cent. zinc is soluble in magnesium at this temperature. All structural changes are in good agreement with the hardness

[10] *Op. cit.*

[11] R. Chadwick: The Constitution of the Alloys of Magnesium and Zinc. *Jnl.* Inst. Met. (1928) **39,** 285.

[12,13] *Op. cit.*

FIGS. 36–43.—(Captions on opposite page.)

values reported in Table 3. Solution heat treatment softens the alloys; precipitation heat treatment increases the hardness until the precipitated particles are large enough to affect the microstructure, a change that is accompanied by softening.

Magnesium-tin Alloys

The most recent work on these alloys is that of Hume-Rothery,[14] who states that tin is not soluble in magnesium. This conclusion was not verified by our present work. The cast structures in Figs. 30 to 32 all show considerable evidence of coring, a usual accompaniment of non-homogenized solid solution. On solution heat treatment, all traces of coring disappear, while the undissolved eutectic compound in the 8 per cent. alloy is completely globularized (Fig. 33).

Precipitation at 150° C. is without marked effect on the structure of the solution-heat-treated specimens (Fig. 34). Precipitation for a longer time at a higher temperature, 250° C., resulted in the structure shown in Fig. 35, which is similar to Fig. 17 in the magnesium-aluminum series. This treatment (−37) also caused a slight but definite hardening on alloys containing more than 4 per cent. tin, as shown in Table 3. Further treatment at still higher temperatures produced no additional changes, either in hardness or microstructure.

While much work remains before definite conclusions can be drawn, we believe that the data obtained point to a limited solubility of tin in magnesium—perhaps 3 to 4 per cent. at the eutectic temperature.

Magnesium-manganese Alloys

Published statements dealing with the magnesium-manganese alloys are extremely few. Schmidt[15] states that up to 4 per cent. manganese

[14] W. Hume-Rothery: Researches on Intermetallic Compounds. *Jnl.* Inst. Met. (1926) **35,** 336; *ibid.* (1927) **38,** 127.

[15] *Op. cit.*

Fig. 36.—Mg-0.1 Mn, No. 4409. × 200. Chill cast. Etched 2 per cent. $H_2C_2O_4$.

Fig. 37.—Mg-0.4 Mn, No. 4411. × 200. Chill cast. Etched 2 per cent. $H_2C_2O_4$.

Fig. 38.—Mg-1 Mn, No. 4412. × 200. Chill cast. Etched 2 per cent. $H_2C_2O_4$.

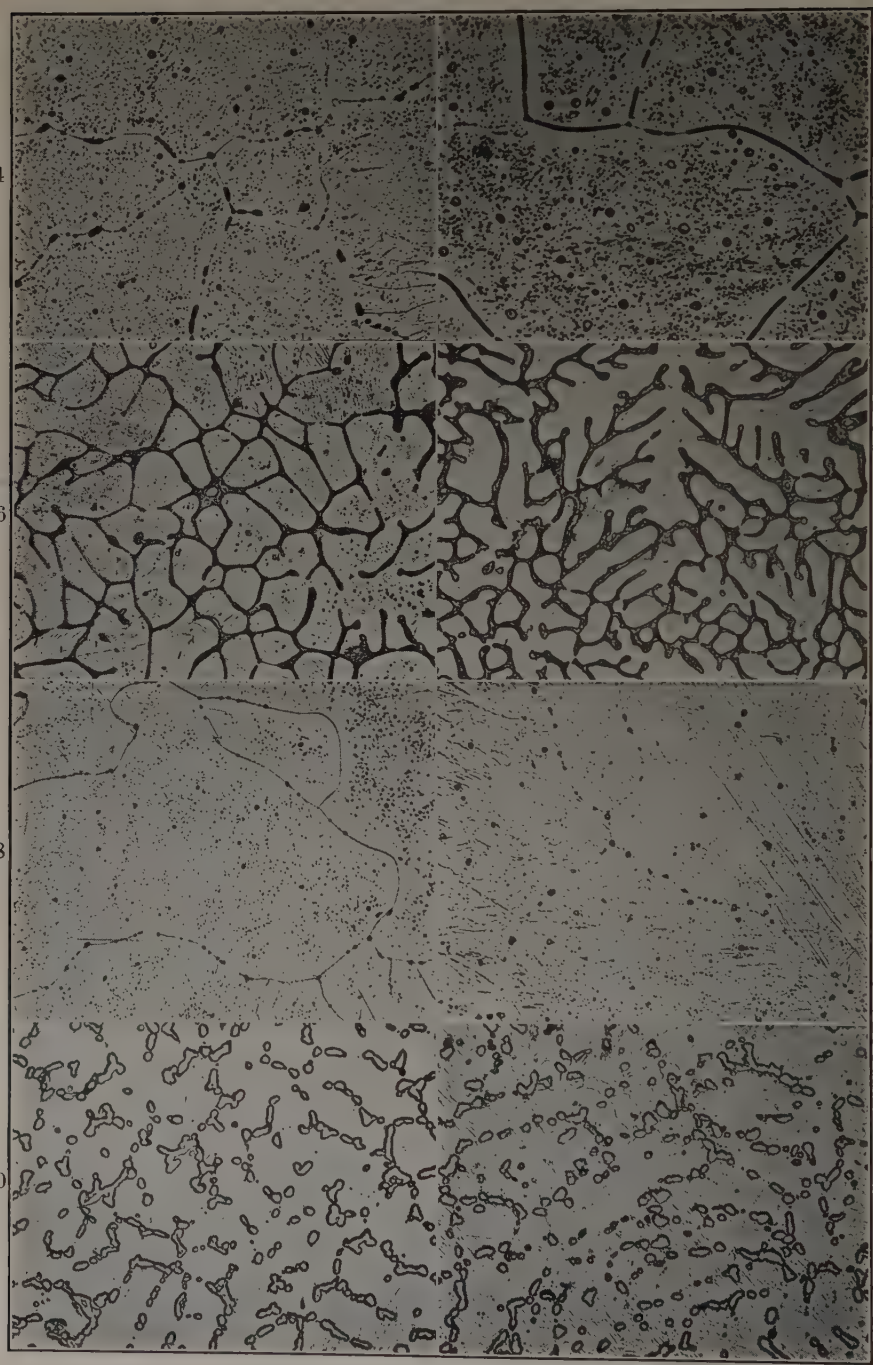
Fig. 39.—Mg-1 Mn, No. 4412. × 200. Chill cast. Etched 2 per cent. HNO_3.

Fig. 40.—Mg-0.1 Mn, No. 4409–30. × 200. Solution heat treatment. Etched 2 per cent. $H_2C_2O_4$.

Fig. 41.—Mg-0.1 Mn, No. 4409–32. × 200. Precipitated at 150° C. Etched 2 per cent. $H_2C_2O_4$.

Fig. 42.—Mg-1 Mn, No. 4412–30. × 200. Solution heat treatment. Etched 2 per cent. $H_2C_2O_4$.

Fig. 43.—Mg-1 Mn, No. 4412–32. × 200. Precipitated at 150° C. Etched 2 per cent. $H_2C_2O_4$.



FIGS. 44–51.—(Captions on opposite page.)

alloys with magnesium. He believes that it is present as an intermetallic compound and that neither eutectic nor solid solution is formed. His conclusions relative to intermetallic compound and solid-solution formation do not seem warranted, in view of the limited data submitted. On the other hand, Bakken and Wood[16] say "an alloy containing 3.2 per cent. manganese shows the typical structure associated with homogeneous alloys."

In the cast state, some manganese is present as a solid solution, but chiefly as small blue-gray particles scattered throughout the primary magnesium crystals, occasionally in clusters but seldom at the boundaries (Fig. 39). The amount that will alloy with magnesium depends on the amount of other alloying ingredients present, the effect of these other metals being to decrease the amount of manganese retained in the alloy. Based on alloying experiments and settling tests on the molten metal, we feel that these particles are elementary manganese rather than an intermetallic compound. Individual particles have been observed in cast alloys containing as little as 0.01 per cent. manganese.

The structures of the cast alloys containing 0.1, 0.4, and 1.0 per cent. manganese are shown in Figs. 36 to 38. These photographs show a small amount of coring around the individual particles due to solid solution, and indicate that the location of the manganese particles is closely associated with the original dendritic structure of the primary crystallization.

Solution heat treatment substantially removes all traces of the coring present in the cast structures but develops the fine detail shown in Figs. 40 and 42. Precipitation heat treatment produces but little additional change (Figs. 41 and 43). This may indicate that the rate of precipitation of the manganese has been so great that some took place even on the quenched solution-heat-treated specimens. This conclusion is further substantiated by the fact that precipitation heat treatment caused no increase in hardness.

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[16] Bakken and Wood: Constitution of Magnesium-manganese Alloys. A. S. S. T. Handbook, 1929 Ed., 560.

FIG. 44.—MG-0.25 CU, No. 4397. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.

FIG. 45.—MG-1 CU, No. 4399. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.

FIG. 46.—MG-4 CU, No. 4401. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.

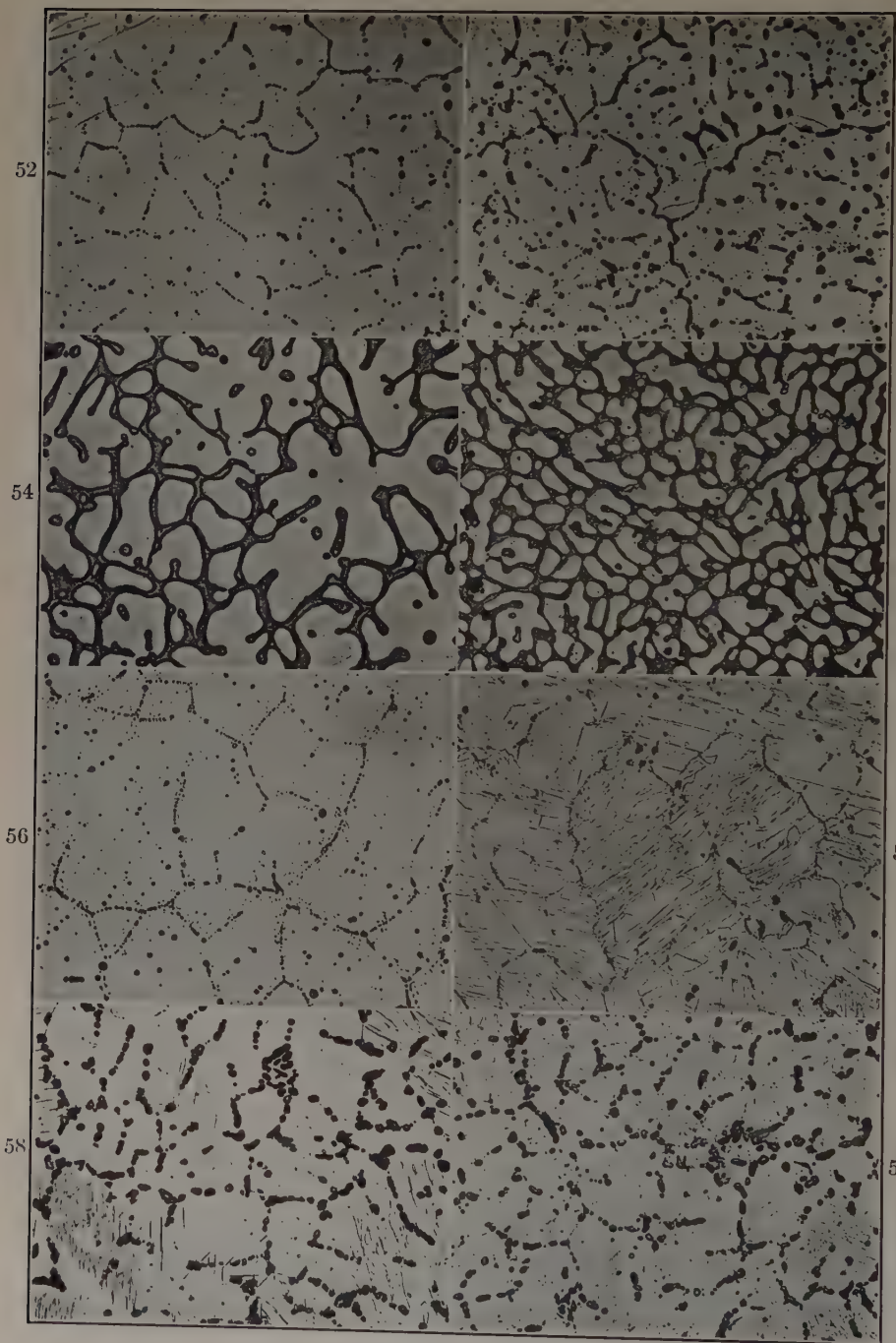
FIG. 47.—MG-8 CU, No. 4402. × 200. CHILL CAST. ETCHED 2 PER CENT. HNO_3.

FIG. 48.—MG-0.25 CU, No. 4397–30. × 200. SOLUTION HEAT TREATMENT. ETCHED 2 PER CENT. HNO_3.

FIG. 49.—MG-0.25 CU, No. 4397–32. × 200. PRECIPITATED AT 150° C. ETCHED 2 PER CENT. HNO_3.

FIG. 50.—MG-8 CU, No. 4402–30. × 200. SOLUTION HEAT TREATMENT. ETCHED 2 PER CENT. HNO_3.

FIG. 51.—MG-8 CU, No. 4402–32. × 200. PRECIPITATED AT 150° C. ETCHED 2 PER CENT. HNO_3.



FIGS. 52–59.—(Captions on opposite page.)

Magnesium-copper Alloys

The recent work on these alloys by Jones[17] gives little indication of the solubility limits of copper in magnesium. That these are low is indicated in Fig. 44 on the cast 0.25 per cent. alloy. In addition to the compound isolated on the grain boundaries, there is a considerable amount scattered throughout the groundmass as very small black particles. The higher percentage alloys have a smaller grain size and a much clearer groundmass on account of the coalescence of the small particles into the larger masses of the network eutectic (Figs. 45 to 47). As the amount of compound increases, the detail within the particles improves, and above 4 per cent. copper approximates a true eutectic structure.

Solution heat treatment of the 0.25 per cent. copper alloy dissolved most of the larger particles of compound (Fig. 48). The small dots remaining in the groundmass probably indicate a precipitation rate in excess of the rate of quenching. This is confirmed by the precipitated sample (Fig. 49), which is quite similar to the solution-heat-treated sample, except for the stronger development of twins. Solution heat treatment of the 1 per cent. alloy left much of the compound as globular masses. Therefore Hansen's[18] conclusion that copper has a solubility at room temperature of 0.1 per cent., and of about 0.5 per cent. at 485° C., is at least approximately accurate.

Heat treatment of the higher percentage alloys results in globularizing the compound with loss of the network eutectic structure (Fig. 50). Jones attributes this change to forging, stating that heat treatment simply increases the size of the globules. Precipitation of the 8 per cent. alloy was without effect beyond the development of twins (Fig. 51).

In confirmation of the microstructural observations, no age-hardening effects were noticed on any of the compositions. The slight reduction in hardness on the solution-heat-treated samples is probably due to the globularizing of the eutectic and the breaking down of the network structure.

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[17] W. R. D. Jones: The Copper-magnesium Alloys, Part III. *Jnl.* Inst. Met. Advance Copy No. 469 (1928).

[18] M. Hansen: Note on the Magnesium-rich Magnesium-copper Alloys. *Jnl.* Inst. Met. (1927) **37**, 93.

Fig. 52.—Mg-0.25 Ni, No. 4403. × 200. Chill cast. Etched 2 per cent. HNO_3.
Fig. 53.—Mg-1 Ni, No. 4405. × 200. Chill cast. Etched 2 per cent. HNO_3.
Fig. 54.—Mg-4 Ni, No. 4407. × 200. Chill cast. Etched 2 per cent. HNO_3.
Fig. 55.—Mg-8 Ni, No. 4408. × 200. Chill cast. Etched 2 per cent. HNO_3.
Fig. 56.—Mg-0.25 Ni, No. 4403-30. × 200. Solution heat treatment. Etched 2 per cent. HNO_3.
Fig. 57.—Mg-0.25 Ni, No. 4403-32. × 200. Precipitated at 150° C. Etched 2 per cent. HNO_3.
Fig. 58.—Mg-4 Ni, No. 4407-30. × 200. Solution heat treatment. Etched 2 per cent. HNO_3.
Fig. 59.—Mg-4 Ni, No. 4407-32. × 200. Precipitated at 150° C. Etched 2 per cent. HNO_3.

Magnesium-nickel Alloys

These alloys are similar to those of the magnesium-copper series in their general characteristics. The grain size decreases on the cast specimens with increasing nickel content (Figs. 52 to 55). The eutectic develops a network structure with some improvement in the internal detail.

Heat treatment of the 0.25 per cent. alloy results in but slight, if any, solution of the compound as shown in Fig. 56. Precipitation of the solution-heat-treated material produces no change beyond the accentuation of the twin needles. This is confirmed by the absence of age-hardening. The network eutectic of the higher percentage alloys is broken down, and the compound globularized by solution heat treatment (Fig. 58), with a slight decrease in hardness. Here again the only effect of precipitation heat treatment is to strengthen the twin needles (Fig. 59).

Summary

1. The preparation and metallography of magnesium-alloy specimens have been described, and an explanation offered for the structures developed.

2. Solution and precipitation heat treatment produce structural changes in most magnesium alloys which are not necessarily accompanied by property changes.

3. Property improvement due to heat treatment occurs in the magnesium-aluminum, magnesium-zinc, and to a limited extent in the magnesium-tin alloys, where hardness increases of 45, 55, and 8 per cent. respectively were observed after precipitation heat treatment.

4. The most pronounced property change in the other alloys occurred in the magnesium-copper and magnesium-nickel series, where solution heat treatment caused a softening due to a globularization of the network eutectic.

5. No definite conclusions have been drawn relative to the limits of solid solution. This more detailed work will form the basis of future investigations.

Acknowledgment

The author wishes to express his appreciation to the members of the metallurgical staff of The Dow Chemical Co. for their assistance in this investigation.

Stability of Aluminum and Magnesium Casting Alloys

By A. J. Lyon,* Dayton, Ohio

(Philadelphia Meeting, October, 1928)

The stability and permanence of any structural material used in aircraft are of paramount importance. The spontaneous hardening, or age-hardening, which takes place in some of the aluminum alloys under ordinary conditions of temperature and atmosphere, is accompanied by an increase in tensile strength and proportional limit and a decrease in elongation or ductility. Within the last few years the introduction of a number of strong and ductile casting alloys led to a study by the Materiel Division, Air Corps, of the permanence of the physical properties in several of these alloys. It has been found that even though some alloys have good properties directly after casting or heat treatment, they are not satisfactory for stressed parts that require a combination of strength and ductility. It has also led to the conclusion that all alloys that can be hardened by artificial aging—heating in a temperature range below 170° C. (340° F.)—will harden spontaneously if allowed to stand for a sufficient length of time. It follows that, in aircraft work where the factors of safety are limited on account of the necessity of keeping the weight of the structures as low as possible consistent with their safe operation, the properties of the alloys in the stable or final condition should be used as a basis for design rather than the properties obtained on the material directly after casting.

The work of Wilm in Germany, Hanson and Gayler at the National Physical Laboratory in England, and Merica, Jeffries, and others in the United States, has shown that the spontaneous hardening is characteristic to a greater or less extent in all aluminum-base alloys in which the solubility in the solid state of the alloying constituents decreases with the temperature. It has been shown that, by heating to a temperature as near as possible to the melting point of the material and soaking at that temperature for a sufficient length of time and then quenching or cooling rapidly, a maximum amount of the soluble constituents can be retained in solution and the condition of maximum hardening effect upon aging can be obtained. Also, in ordinary sand and chill castings, without heat treatment, a sufficient amount of the alloying constituents is held in solution to cause important changes in the final physical properties.

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* First Lieutenant, Air Corps, U. S. Army.

The theory of spontaneous hardening as evolved by Merica is based on the soluble constituents separating out in submicroscopic particles when the material is allowed to stand at ordinary temperatures. The impression gained from the literature on the subject is that the most important changes take place in a comparatively short time after casting or heat treatment. The scope of this paper is to show that this is not the case for all aluminum and magnesium-base alloys and that in some cases the hardening continues over a period of two or more years. It also points to the possibility that all materials subject to spontaneous aging can be artificially aged in a few hours. When artificially aged, the properties are stable and represent the final properties of the material attained by aging naturally for a period of several years. In other words, the rate of hardening is a function of temperature in the range 0° to 260° C. (32° to 500° F.).

The following types of sand-cast alloys were investigated:

1. Aluminum-base
   - *a.* Aluminum-copper
   - *b.* Aluminum-copper-magnesium
   - *c.* Aluminum-copper-nickel-magnesium
   - *d.* Aluminum-silicon
   - *e.* Aluminum-zinc
2. Magnesium-base
   - *a.* Magnesium-aluminum-manganese
   - *b.* Magnesium-aluminum-zinc

Method of Test

The test specimens were of the types and dimensions shown in Fig. 1. They were cast in greensand and ordinary foundry practice was observed in the molding, gating, melting, and pouring. The molding sand used for casting the magnesium-base alloys contained from 3 to 5 per cent. of flowers of sulfur with a small amount of boric acid to prevent reaction between the water used for tempering and the molten metal. All melting was done in crucible-type furnaces. For the aluminum-base alloys, plumbago or graphite crucibles were used; and for the magnesium-base alloys, cast-iron crucibles. Fluxes were not employed. The pouring temperature was maintained in the temperature range of 1275° to 1325° F. The maximum furnace temperature was not allowed to exceed the pouring temperature more than 75° F. This is of considerable importance, as it has been shown that the temperature of pouring and the size of the cast section have a considerable effect on the grain size of both the aluminum and magnesium-base alloys. It also is of special importance in connection with the newer types of alloys that require heat treatment to develop their maximum properties, since the coarser the structure, the longer the time required for solution of the soluble constituents. Incomplete

solution has a very decided effect on the ductility as measured by the percentage of elongation, the maximum corresponding to complete solution. In the aluminum-copper alloys in the heat-treated condition, a variation of 200° F. in the pouring temperature causes variations in the ultimate strength of 15 per cent. and in the elongation of 40 per cent.[1] In the range of pouring temperatures used in this investigation, the effect on the properties is not of importance. The test specimens shown in Fig. 1 are ½ and ⅞ in. dia. over the reduced section. The effect of the size of the section is more pronounced on the ductility than on the ulti-

Fig. 1.—Test specimens.

mate strength, and these factors, together with the method of gating, should be borne in mind when comparing results of this investigation with other published data.

The chemical composition was determined in all cases on the original melts from which the material used in the test specimens was selected. Slight variations therefore can be expected between the tabulated chemical composition and the actual chemical composition of each individual specimen.

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[1] Private communication from the Research Department, Aluminum Co. of America.

Unless otherwise stated, the specimens were all aged under ordinary conditions at atmospheric temperature and were stored under cover. The magnesium alloy specimens subjected to outdoor exposure were placed on racks at an angle of 45° and faced southwest, and were subjected to the atmospheric conditions of temperature and moisture in Dayton, Ohio.

The Type TB-1 specimens, cast to size ½-in. dia. over a 2-in. gage length, were tested in a 20,000-lb. Olsen machine fitted with self-aligning wedge grips. The ultimate strength was calculated on the basis of the average cross-sectional area over the gage length. The elongation was measured with dividers on the broken specimen to the nearest 1/100 in. The Brinell hardness tests were made on the tension specimen by grinding flats on the shoulders. A 10-mm. ball and a 500-kg. load for 30 sec. were employed in all cases. The impressions were measured by a micrometer microscope.

The Type TB-14 specimens (Fig. 1), used for determining the proportional limit, were machined from ⅞-in. dia. to ¾-in. dia. over a gage length of 8 in. (The removal of the skin in casting aluminum alloys slightly decreases the tensile properties and should also be taken into consideration in comparing the results obtained from the two types of specimens). The ends of the specimens were threaded to fit adapters. The specimens were then pulled in an Olsen 20,000-lb. machine fitted with self-aligning pulling bolts. The loads were applied in increments of 200 lb., and for each load a corresponding strain over a gage length of 8 in. was read on a direct-reading Ewing extensometer calibrated to read directly to 0.0002 in. This is equivalent to 0.000025 in. per inch. These results were plotted to a scale of 1 in. = 500 lb. and 1 in. = 0.00025 in. per inch, and the proportional limit determined by taking the point where the curve first changes slope. The ultimate strength was calculated from the breaking load and the percentage of elongation was determined by measurements on the broken specimen over a gage length of 2 in. Extreme care was taken in the proportional limit determinations for the reason that it has been found that the stress-strain diagrams afford a very accurate means of obtaining information for the study of changes in properties resulting from age-hardening and furnish more reliable data than ultimate strength, Brinell hardness, and ductility tests. In a recent publication of the Bureau of Standards,[2] attention is directed to the fact that the yield point is not a definite property, as in steel, and that much of the existing data in the literature fail to disclose the method of determining this property. The introduction of the casting alloys of high tensile strength and ductility has created the necessity for accurate determinations of the yield point or proportional limit.

[2] Light Metals and Alloys—Aluminum, Magnesium. U. S. Bur. of Stds. *Circ.* 346 (1927).

Aluminum-copper Alloys

The effects of aging at atmospheric temperatures on the 8 per cent. and 5 per cent. binary aluminum-copper alloys are shown in Tables 1 and 2 and in Figs. 2 and 3. The first is the well-known S. A. E. alloy No. 12 and is used extensively in aircraft construction for the general run of castings. The proportional limit of this alloy is practically doubled and appreciable changes take place in the ultimate strength after two years'

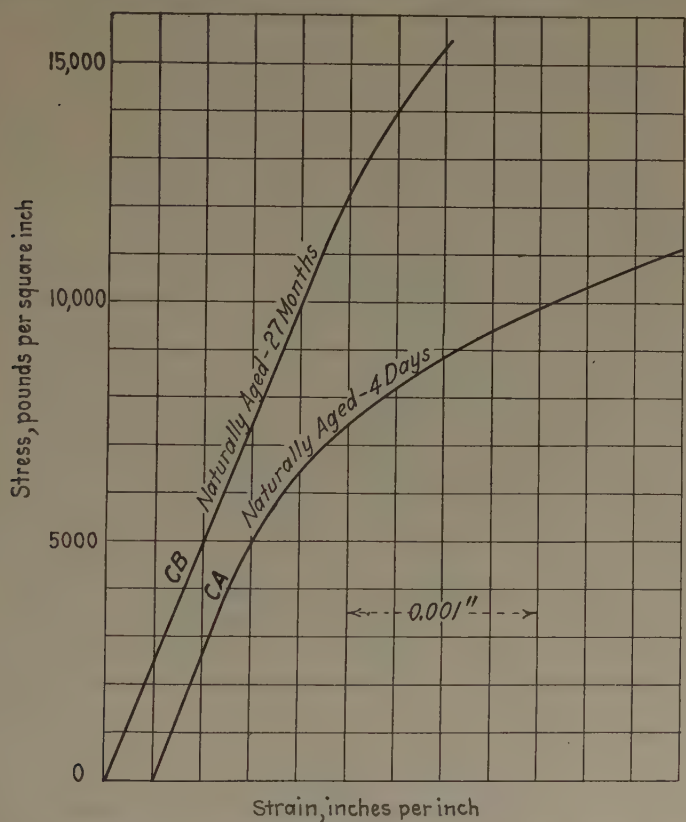

Fig. 2.—Stress-strain diagram, sand-cast alloy; 8 per cent. copper, 92 per cent. aluminum.

aging at atmospheric temperature. The percentage of elongation of the alloy in the cast condition is so low that accurate comparisons cannot be made. It has been found that when this alloy is artificially aged at a temperature of 300° F. for 16 hr. practically the same changes in ultimate strength as are shown in Table 1 are obtained in the material in the as-cast condition.

The second of the Al-Cu alloys is a proprietary alloy known as Lynite No. 195, which should be distinguished from the sand-cast duralumins

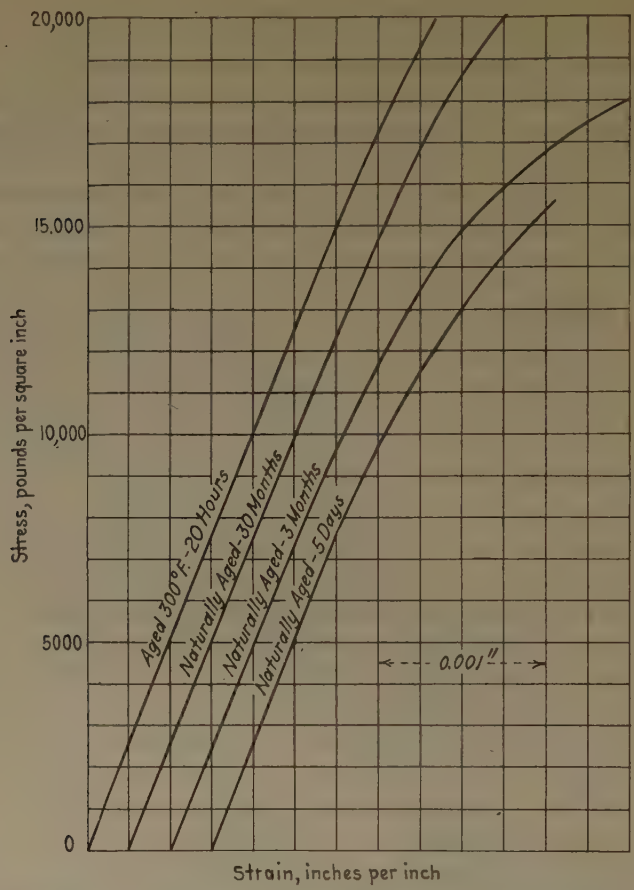

FIG. 3.—STRESS-STRAIN DIAGRAM, SAND-CAST HEAT-TREATED ALLOY; 5 PER CENT. COPPER, 95 PER CENT. ALUMINUM. HEATED 24 HR. AT 950° F.; QUENCHED IN WATER.

TABLE 1.—*Data on Sand-cast Aluminum-copper Alloy Naturally Aged*

Physical Properties	Time	Aged	Chemical Composition	Per Cent.
	14 Days	27 Months		
Proportional limit, lb. per sq. in.	4,600	10,500	Copper	8.05–8.12
Ultimate strength, lb. per sq. in.	17,480	23,270	Iron	0.40–0.57
Elongation in 2 in., per cent.	<1.0	<1.0	Silicon	0.36–0.37
Brinell hardness	62	78	Aluminum	Difference

Type of specimen, TB-14; cast ⅞-in. dia.; machined ¾-in. dia.; gage length, 8 in.

TABLE 2.—*Data on Sand-cast Aluminum-copper Alloy Heated at 950° F. for 24 Hr.; Quenched in Cold Water*

Physical Properties	Aging Temperature and Time					Chemical Composition	Per Cent.
	Atmospheric			300° F.			
	5 Days	3 Mo.	30 Mo.	2 Hr.	20 Hr.		
Proportional limit, lb. per sq. in.	7,075	9,920	13,625	11,615	15,825	Copper	4.93
Ultimate strength, lb. per sq. in.	28,135	26,980	29,830	31,155	35,915	Iron	0.62
Elongation in 2 in., per cent	3.7	2.6	1.2	3.0	1.25	Silicon	0.84
Brinell hardness (500 kg. 10-mm. ball)	74	70	80	75.1	84.1	Manganese	0.03
						Aluminum	Difference

Type of specimen, TB-14; cast 7/8-in. dia.; machined 3/4-in. dia.; gage length, 8 in.

that contain small amounts of magnesium. Both are used in aircraft and aircraft engines for parts that are subjected to high stresses and where forgings are impracticable. The straight copper alloy is regarded with more favor than the duralumin-type alloy on account of the better combination of strength and ductility. An examination of Fig. 3 shows that the natural age-hardening continues over a period of 2½ years, the proportional limit then approaching that of the same material artificially aged at 300° F. for a period ranging from 2 to 8 hr. After 20 hr. artificial aging at this temperature, the final properties of the alloy are approached. Artificial aging for this type of alloy has been made mandatory by the Air Corps principally on account of the increase in proportional limit. The elongation obtained on the unaged material is misleading. Although the elongation is reduced practically 50 per cent. by artificial aging, the ductility is superior to the duralumin-type and the higher copper alloys. Former work done by the Engineering Division of the Air Service on the cast alloys of the duralumin-type and on the binary aluminum-copper alloys[3] shows that the alloys containing small amounts of magnesium harden more rapidly than the straight copper alloy and, when artificially aged, reach their maximum after about 20 hr. at 300° F. The latter show a gradual increase in ultimate strength up to 160 hr., but at 24 hr. the maximum is reached for all practical considerations.

The effect of aging, either spontaneously or artificially, on the wrought alloys of the duralumin type is more pronounced and the time shorter than for the cast alloys of the same composition.[4] The results shown in Fig. 3 would indicate that, if careful determination of the proportional

[3] S. Daniels, A. J. Lyon and J. B. Johnson: Casting and Heat Treatment of Some Aluminum-copper-magnesium Alloys. *Trans.* (1925) **71**, 864.

[4] R. S. Archer and Zay Jeffries: New Developments in High-strength Aluminum Alloys. *Trans.* (1925) **71**, 828.

limit is made on the wrought binary aluminum-copper alloy, quenched, and allowed to age at ordinary temperatures, the increase in proportional limit would be of the same order but would take place in a shorter period of time. This is important in connection with the "stocking" of this alloy in the as-quenched condition and then after a period of a year or two subjecting it to forming or severe bending operations in connection with the fabrication processes.

Aluminum-copper-magnesium Alloys

The 10 per cent. copper alloy with small additions of iron and magnesium is used extensively in manufacture of aircraft engines, for such parts as pistons and air-cooled cylinder heads, and in other places where high strength and hardness are necessary but the ductility is not important. It is used in both the heat-treated and as-cast conditions. Table 2 shows that in the as-cast condition the alloy reaches a stable condition after about one year at ordinary temperatures. In the quenched condition, aging for 16 hr. at 300° F. produces the maximum properties and no further hardening or increase in proportional limit takes place. The effect of increasing the time of artificial aging for periods longer than 16 hr. has been shown to produce no appreciable changes in the physical properties.[5] An increase in the artificial aging temperature decreases the time required to obtain the maximum properties to a considerable degree. At temperatures from 400° to 500° F., the same results can be obtained in periods of 1 hr. or less as for 16 hr. at 300° F.

The alloy containing 2.5 per cent. copper and 0.5 per cent. magnesium, which is a duralumin-type alloy, has been used by the Air Corps as a high-strength alloy in the heat-treated condition and in the as-cast condition for purposes where a combination of strength and ductility greater than that obtained in the 8 per cent. copper alloy is required. The ultimate strength and elongation vary within wide limits for different melts of the alloy of practically the same composition, cast under the same conditions. The results in Table 4 are representative of the maximum rather than of the average properties, but are included to show the effect of aging at ordinary temperatures over a period ranging from two days to 3½ yr. The effect of magnesium, as mentioned before, is to decrease the time required for the alloy to reach its stable condition. During the first two weeks, the hardening progresses rapidly and then slowly up to about a year. The results tabulated for periods greater than a year are within the range of properties obtained from different specimens from the same heat and aged for the same length of time. The tests on TB-14 speci-

[5] S. Daniels: Effect of Reheating Al-Cu-Ni-Mg and Al-Cu-Fe-Mg Alloys. *Trans.* (1926) **73**, 479.

mens, which have not been included in Table 4, gave an ultimate strength of 24,000 lb. per sq. in., a proportional limit of 8000 lb. per sq. in., and an elongation of less than 1 per cent. These properties should be compared

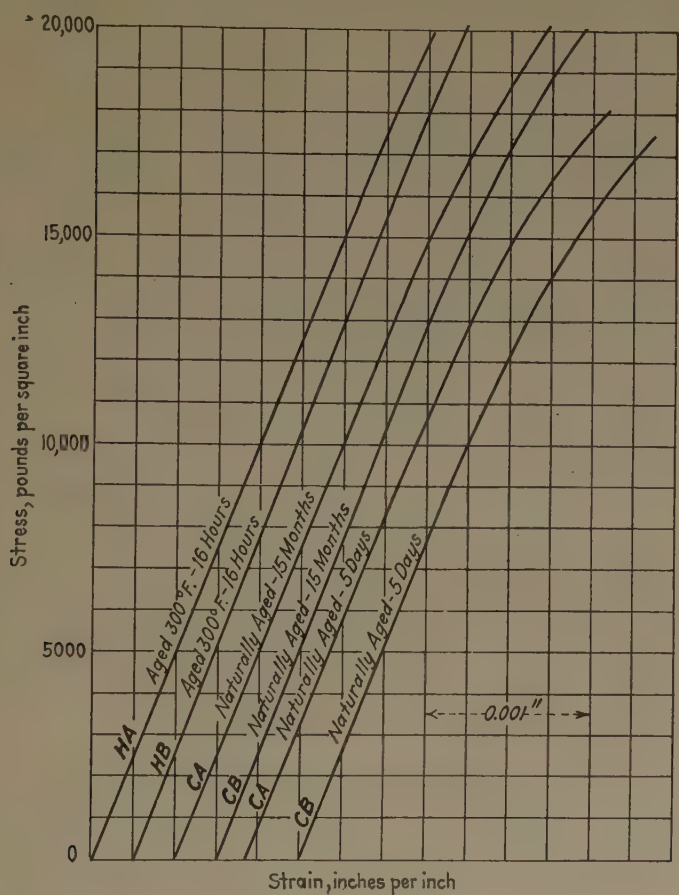

FIG. 4.—STRESS-STRAIN DIAGRAM, ALUMINUM-COPPER-NICKEL AND ALUMINUM-COPPER-MAGNESIUM ALLOYS.

Alloy A = Cu, 4 per cent.; Mg, 1.5; Al, remainder.
Alloy B = Cu, 10 per cent.; Fe, 1.25; Mg, 0.25; Al, remainder.
HA = heat-treated 5 hr. at 950° F.
HB = heat-treated 5 hr. at 925° F.
CA and CB = as cast

with those given for the 5 per cent. aluminum-copper alloy, Table 2. This alloy furnishes a good example of the misleading results that can be obtained from alloys of this type if not properly aged before testing.

TABLE 3.—*Data on Sand-cast Aluminum-copper-magnesium-iron Alloy Naturally Aged*

Physical Properties	Condition and Aging Time					Chemical Composition	Per Cent.
	As-cast			Heat-treated[a]			
	5 Days	15 Mo.	28 Mo.	5 Days	28 Mo.		
Proportional limit, lb. per sq. in.	7,920	10,550	10,500	15,030	15,800	Copper	9.65
Ultimate strength, lb. per sq. in.	20,890	22,135		25,860	28,600	Iron	1.38
Elongation in 2 in., per cent			Less than	1.0		Silicon	0.39
Brinell hardness	88	97	99	110	105	Magnesium	0.28
						Aluminum	Difference

Type of specimen, TB-14; cast ⅞-in. dia.; machined ¾-in. dia.; gage length, 8 in.

[a] Soak 925° F. for 5 hr.; quench in water; age 16 hr. 300° F.

TABLE 4.—*Data on Sand-cast Aluminum-copper-magnesium-iron Alloy Naturally Aged.*

Physical Properties	Time Aged					Chemical Composition	Per Cent.
	2 Days	14 Days	11 Mo.	23 Mo.	43 Mo.		
Ultimate strength, lb. per sq. in.	26,530	29,460	31,940	28,088	30,400	Copper	2.59–2.66
Elongation in 2 in., per cent	4.8	4.0	3.5	2.63	3.5	Iron	1.47–1.55
Brinell hardness	57	65	73	71		Silicon	0.17–0.22
						Magnesium	0.54–0.60
						Aluminum	Difference

Type of specimen, TB-1; cast to size ½-in. dia.; 2-in. gage length.

ALUMINUM-COPPER-NICKEL-MAGNESIUM ALLOYS

The physical properties of the alloy containing 4 per cent. copper, 2 per cent. nickel, and 1.5 per cent. magnesium are practically of the same order as those of the copper-magnesium alloy just described. It is commercially known as "Y" alloy and there are also a number of compositions with somewhat the same properties which are known as Magnalite. Table 5 shows that it is in a stable condition after aging at 300° F. for 16 hr. Like the copper-magnesium alloy, however, the same results can be produced by shorter reheating periods at a higher temperature; 500° F. appears to be the upper limit of the reheating range for this alloy. In the as-cast condition the principal change upon aging at atmospheric temperature occurs in the proportional limit. The alloy appears to be more stable in this condition than the aluminum-copper-magnesium alloy, and the proportional limit directly after casting is appreciably higher. It appears that the improvement in properties by heat treatment is derived from the heating at elevated temperature and the quenching operation

more than from the subsequent aging. This alloy is used for pistons and air-cooled cylinder heads and, although slightly more difficult to cast on account of the higher percentage of magnesium, the improved properties at elevated temperatures such as are met in aircraft engines warrant its use.

Aluminum-silicon Alloys

The aluminum-silicon alloys, which include the normal and modified types, are not subject to spontaneous hardening, or age-hardening. They

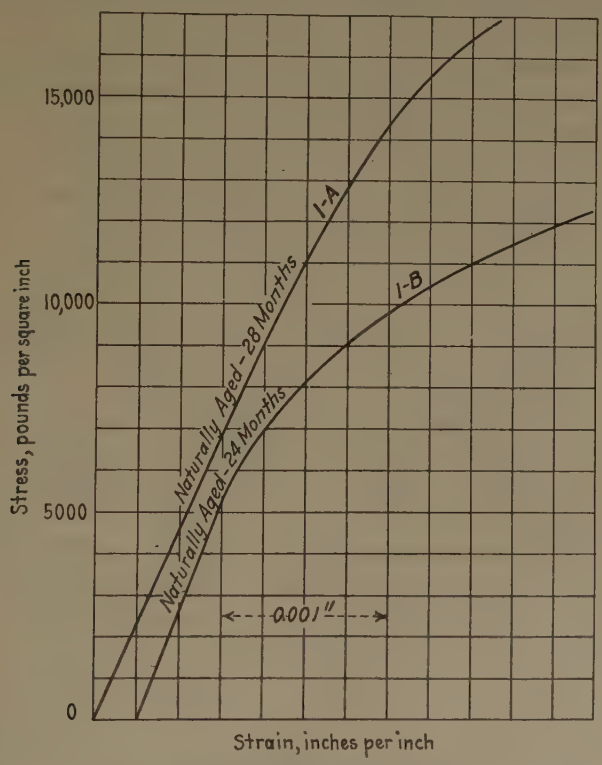

Fig. 5.—Stress-strain diagram, sand-cast silicon-aluminum and copper-magnesium-aluminum alloys..

1-A = Cu, 2.5 per cent.; Fe, 1.25; Mg, 0.25; Al, remainder.
1-B (Alpax) = Si, 13; Al, 87.

are practically stable in the cast condition. In the normal alloy a small improvement of the elongation may be obtained through heat treatment, but no appreciable changes in the ultimate strength or proportional limit take place. In Table 6 are shown results of tests made after 3 months and 2 years aging, respectively, at atmospheric temperature, on a commercial grade of the modified alloy, which corresponds to Alpax metal in the United States and to Silumin abroad. The physical properties listed

are within the range obtained on individual test specimens from the same lot of metal and tested under the same conditions. In passing, it should be observed that, although this type of alloy has an attractive combination of ductility and ultimate strength, the proportional limit is very low and should prevent the alloy being placed in the class of the high-strength alloys. The Air Corps has attempted to use this material for important and highly stressed fittings, such as control fittings and landing-gear fittings. There are records of failures resulting from the gradual stretching and distortion of the part due to suddenly applied loads above the proportional limit but well under the ultimate strength. A typical stress-strain diagram for this alloy is shown in Fig. 5. For the purpose of comparison, a diagram of the low-copper, duralumin-type alloy in the as-cast condition is also shown. These should be compared with the stress-strain diagrams of Fig. 3.

TABLE 5.—*Data on Sand-cast Aluminum-copper-nickel-magnesium Alloy Naturally Aged*

Physical Properties	Condition and Aging Time					Chemical Composition	Per Cent.
	As-cast			Heat-treated[a]			
	5 Days	11 Mo.	27 Mo.	5 Days	28 Mo.		
Proportional limit, lb. per sq. in.	9,337	13,730	12,200	14,140	13,580	Copper	4.13–4.44
						Nickel	1.52–1.79
Ultimate strength, lb. per sq. in.	25,545	25,805	24,235	28,950	30,840	Iron	0.22–0.58
						Magnesium	1.51–1.56
Elongation in 2 in., per cent	Less than 1.0					Silicon	0.15–0.24
						Aluminum	Difference
Brinell hardness	88		88	97	102		

Type of specimen, TB-14; cast ⅞-in. dia.; machined ¾-in. dia.; gage length, 8 in.
[a] Heat 950° F. for 5 hr.; quench in cold water; age at 300° F. for 16 hr.

TABLE 6.—*Data on Sand-cast Modified Aluminum-silicon Alloy Naturally Aged*

Physical Properties	Time Aged		Chemical Composition	Per Cent.
	3 Mo.	24 Mo.		
Proportional limit, lb. per sq. in.	3,700	4,275	Silicon	13
			Aluminum	87
Ultimate strength, lb. per sq. in.	24,975	26,110	Modified (Pacz Method)	
Elongation in 2 in., per cent.	5.38	4.09		
Brinell hardness	60.0	59.4		

Type of specimen, TB-14; cast ⅞-in. dia.; machined ¾-in. dia.; gage length, 8 in.

Aluminum-zinc Alloys

The binary aluminum-zinc alloys are not recommended for use in aircraft, but there are several combinations of zinc, copper, and aluminum that have found their way into aircraft engines on account of the good combination of strength and ductility which can be obtained without heat treatment. The results shown in Table 7 indicate that the 15 per cent. aluminum-zinc alloy is unstable and the ultimate strength increases 50 per cent. after 2 years aging at atmospheric temperature. This increase in ultimate strength, however, is accompanied by a loss of ductility of such magnitude that it would prevent the alloy being used for purposes where ductility is important. The change in properties of the aluminum-zinc alloy is the one exception in the commercial alloys referred to in this paper in which the hardening effect is not due to the decrease of the solid solubility of the alloying constituent with temperature. It is probable that the hardening is a result of a phase change and that the reaction[6] that takes place at approximately 256° C. (492° F.) proceeds slowly at ordinary temperatures. It has been stated that the addition of copper does not affect the temperature of this reaction,[7] so that the

Table 7.—*Data on Sand-cast Aluminum-zinc Alloys Naturally Aged*

Physical Properties	Time Aged			Chemical Composition	Per Cent.
	1 Day	9 Mo.	20 Mo.		
Ultimate strength, lb. per sq. in.	20,850	26,460	30,215	Zinc	14.85
Elongation in 2 in., per cent	5.0	1.2	1.5	Iron	0.46
Brinell hardness	50.0		65.0	Silicon	0.45
		—		Aluminum	Difference

Type of specimen, TB-1; cast to size ½-in. dia.; gage length, 2 in.

Table 8.—*Data on Sand-cast Magnesium-aluminum-manganese Alloy Naturally Aged*

Physical Properties	Time Aged				Chemical Composition	Per Cent.
	1 Day	7 Days	13 Mo.	32 Mo.[a]		
Ultimate strength, lb. per sq. in.	24,086	25,820	24,415	22,184	Aluminum	4.58
Elongation in 2 in., per cent	6.7	8.0	6.7	6.2	Copper	0.05
Brinell hardness	45	45	46	44.3	Iron	0.05
					Manganese	0.3
					Silicon	0.03
					Magnesium	Difference

Type of specimen, TB-1; cast round, ½-in. dia.

[a] Specimens exposed to weather at Dayton, Ohio.

[6] W. Rosenhain: *Jnl.* Inst. of Metals (1911) **6**, 248.

[7] Eleventh Alloy Research Report, Institution of Mechanical Engineers (1921), 207.

results shown in Table 7 represent what can be expected of all alloys that contain zinc as the principal alloying constituent. In addition to the loss in ductility, this alloy is not suitable for aircraft use on account of its higher specific gravity, nonresistance to corrosion, and weakness at elevated temperatures. It has been dropped from all Air Corps specifications.

TABLE 9.—*Data on Sand-cast Magnesium-aluminum-zinc Alloys Naturally Aged*

Physical Properties	Composition and Time Aged							
	Al, 5.71; Zn, 2.90; Mg, Difference				Zn, 4.94; Al, 3.19; Mg, Difference			
	1 Day	2 Mo.	13 Mo.	34 Mo.[a]	1 Day	2 Mo.	13 Mo.	34 Mo.[a]
Ultimate strength, lb. per sq. in.	20,090	25,180	23,435	23,178	23,666	24,150	26,905	26,255
Elongation in 2 in., per cent	3.2	4.3	4.6	5.0	4.8	4.1	5.2	5.3
Brinell hardness	49	49	50	50	49	50	54	54.2

Type of specimen, TB-1; cast to size, ½-in. dia.; gage length, 2 in.

[a] Exposed to weather conditions of Dayton, Ohio.

MAGNESIUM-ALUMINUM-MANGANESE ALLOYS

On account of the specific gravity, as compared with that of the aluminum-base alloys, the alloys of magnesium offer attractive possibilities for use in aircraft and aircraft engines. The magnesium-aluminum alloys are stable in the as-cast condition. The results of tests on the 4 per cent. aluminum alloy are included in Table 8. Tests have also been performed on the 8 per cent. and 12 per cent. magnesium-aluminum alloys, without manganese, and show stable properties. In Table 8 the ultimate strength as determined from specimens aged out of doors is slightly lower than those aged indoors. This is on account of a slight reduction in cross-sectional area due to corrosion. There is no loss in ductility, however, and the hardness is of the same order.

MAGNESIUM-ZINC-ALUMINUM ALLOYS

The results of tensile tests on specimens with the zinc content ranging from 3 to 5 per cent. and the aluminum content from 5 to 3 per cent. are shown in Table 9. These, unlike the results for the binary magnesium-aluminum alloys, show pronounced aging properties at ordinary temperatures. There is a pronounced improvement in the ultimate strength and a slight increase in ductility. The hardness remains approximately the same. An examination of the equilibrium diagram for the

magnesium-zinc system[8] shows that on the magnesium end of the diagram the solid solubility of the zinc as a compound $MgZn_2$ decreases very rapidly with temperature. It would follow that the principle underlying the hardening of this type of alloy is the same as for the binary aluminum-copper or the aluminum alloys containing magnesium silicide. The results of the aging tests on two types of magnesium-base alloys, shown in Tables 8 and 9, indicate that there is very little choice between them from a practical standpoint. In cast sections neither is appreciably corroded by the atmospheric conditions of Dayton, Ohio, notwithstanding the fact that they recived no protection except the presence of the skin which forms during the casting. These alloys have recently been ncluded in Air Corps specifications.

Acknowledgment

The author wishes to acknowledge the cooperation of J. B. Johnson and D. M. Warner.

DISCUSSION

R. S. Archer, Cleveland, Ohio (written discussion).—Lieutenant Lyon has properly called attention to the fact that the increase in elastic limit is often even more marked than the changes in strength and elongation, and the stress-strain curves which he has given are especially valuable because of the comparative lack of this kind of information.

Advantage is taken of the aging characteristics of aluminum alloys in various fabricating operations. The straightening of castings, for example, may be done more readily shortly after a solution heat treatment or shortly after casting than after the material has become harder due to aging. Other operations in which the same principle is involved are the heading of rivets, coin pressing of forgings, forming of sheet, etc.

The aging characteristics of these alloys may also be used to advantage from the standpoint of service as well as of manufacture. Lieutenant Lyon appears to have come to the conclusion that these products should be artificially aged to a stable condition before being put in service. There are some considerations, however, in favor of putting such materials into service in the softer condition which obtains shortly after manufacture or heat treatment and allowing the age-hardening to take place in service.

The need for ductility in parts intended for severe service is largely to enable the metal to dissipate local concentrations of stress by local yielding. These local concentrations of stress are often due to strains set up in assembly by imperfect fitting and alignment of parts. During the first stages of service, such as the running-in of an engine, the parts become adjusted to one another. During this process, when as a rule the stresses are intentionally kept low, it is desirable that the materials possess the ductility and the low elastic limit that will facilitate these adjustments. After these have been accomplished it is desirable that the material possess high elastic

[8] R. Chadwick: Constitution of the Alloys of Magnesium and Zinc. *Jnl.* Inst. of Metals (1928).

limit to resist the loads of service without permanent deformation. The spontaneous age-hardening which may occur in service is an advantage from this standpoint.

Lieutenant Lyon has come to the general conclusion that all alloys that can be hardened by artificial aging will harden spontaneously if allowed to stand for a sufficient length of time, and that the properties attained by artificial aging represent the final properties that the material would attain by aging naturally for a period of several years. This conclusion seems too broad, as may be illustrated by pointing out that if it were true, all of these alloys would over-age at room temperature.

At the temperatures employed in artificial aging, such as 170° C., hardness and strength increase to a maximum that may be attained within a few days, after which these properties slowly decrease to nearly constant values. The higher the temperature of the artificial aging or precipitation heat treatment, the lower are these values, and if this treatment were carried out at 260° C., which is included within the author's limits, the final properties would be nearly those of the annealed material. It is evident that in the majority of the materials with which we are concerned such a condition would not be realized in any ordinary period of time, if ever. Observations made on heat-treated alloys of the duralumin type, kept at room temperature over a period of 10 years, failed to show any softening. Briefly, then, it seems that no period of natural aging within human experience would produce the same effects as prolonged artificial aging at temperatures up to 260° C., or even up to 170° C. It may also be stated that even for periods of artificial aging less than required for maximum hardening, the combinations of physical properties obtained are often not the same as those which would be obtained by prolonged natural aging.

The 8 per cent. copper alloy referred to at the top of page 337 is apparently S. A. E. alloy No. 30, the designation No. 12 being a trade designation.

In connection with the aging of heat-treated 4 per cent. copper alloy castings (Lynite 195) it may be of interest to give some results showing the effect of natural aging for 16 months. The test bars were heated in boiling water for 30 min. after the solution heat treatment to simulate a few days' natural aging.

Aging	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.
30 min. at 100° C.	32,910	9.1
16 months at room temperature	36,340	4.3

The author's statement at the bottom of page 339 regarding the relative susceptibility of wrought and cast alloys to aging, attributed to Dr. Jeffries and myself, does not quite express our ideas. In fact, we have occasionally observed that castings seem to age either to a greater extent or more rapidly at room temperature than do wrought products of the same composition. This subject, however, is one on which our information is incomplete.

The author's statements regarding the substantial absence of age-hardening in aluminum-silicon alloys are in accord with our own observations. On page 343, however, he states that only a small change in elongation and no appreciable changes in strength or elastic limit result from "heat treatment." This is not correct if the term "heat treatment" is used in the broad sense which would include solution and spheroidizing treatments, by which the properties of aluminum-silicon alloys can be markedly

changed.[9] The elongation of a commercial 5 per cent. silicon alloy sand casting, for example, was increased from 4.5 to 11.5 per cent. by heating 40 hr. at 565° C. and quenching. At the same time the tensile strength was increased from 19,414 lb. per sq. in. to 22,800 lb. per sq. in. In an alloy of about the same silicon content but of higher purity, the elongation was increased from 9.5 to 25.2 per cent. by heating 75 hr. at 565° C. and quenching. The strength was slightly increased at the same time. By cooling slowly instead of quenching, an elongation of 32.5 per cent. was obtained but with greatly decreased strength and hardness.

A. J. Lyon (written discussion).—The author wishes to thank Dr. Archer for his contribution. The information on the effect of heat treatment on the aluminum-silicon alloy and the effect of aging for a long period of time on the duralumin-type alloy is of particular interest.

The suggestion for taking advantage of the aging characteristics of certain of the aluminum alloys to facilitate the fabrication operations on wrought alloys or the straightening operations on cast alloys is a sound one and has been quite generally adopted. However, the high-strength casting alloys, such as those of the duralumin and Lynite 195 type, should be artificially aged following any straightening or forming operations performed on the quenched material at least before the part is placed in service in either aircraft or aircraft engines. It would be undesirable to have any yielding at points of maximum stress, as this would naturally throw out of line various interconnected parts.

The increased values shown in Table 2 for the proportional limit of the 5 per cent. copper-aluminum alloy quenched and aged may then be used by the designer. It is necessary that parts for either aircraft or aircraft engines be artificially aged to produce the physical properties used as a basis of design for the reason that, in large-scale production or in time of an emergency, 90 days after the castings leave the foundry they might be in actual service. In aircraft the factors of safety, or load factors as they are more properly called, have not quite the same significance as the factors of safety in other engineering structures. Actually there is no factor of safety when an airplane is subjected to certain maneuvers or conditions.

In reference to the statement, "All alloys that can be hardened by artificial aging will harden spontaneously if allowed to stand for a sufficient length of time," it has been found that, in all cases where the alloys harden when aged at atmospheric temperature for long periods of time, practically the same properties can be obtained by artificially aging at the proper temperature and for the proper time. It appears from the data available that the *rate* of hardening is primarily dependent on temperature, chemical composition, and condition (chill-cast, sand-cast, wrought). It is also apparent from the information available on this subject that the rate of hardening for any given temperature proceeds more rapidly at first and decreases with continued exposure, and there is a graph on page 243 of the Eleventh Alloy Research Report of the Institute of Mechanical Engineers, 1921, which shows that there is a very rapid increase in the rate of hardening at about 302° C. These facts, with Dr. Archer's results on the duralumin-type alloy aged for 10 years at atmospheric temperature, would indicate that the rate of hardening at ordinary temperatures is such that there is no probability of the aging phenomena going through the complete cycle of hardening and then softening. This paper is concerned only with the portion of the cycle in which hardening occurs, and from a practical standpoint it has been shown that the aluminum alloys that can be hardened artificially will harden naturally and their properties

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[9] Z. Jeffries and R. S. Archer: U. S. Patent No. 1508556.

R. S. Archer, L. W. Kempf and D. B. Hobbs: Heat Treatment of Aluminum-silicon Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 198.

very closely approximate the maximum properties obtained on the artificially aged materials.

The proper designation of the 8 per cent. copper alloy is as corrected by Dr. Archer.

In reference to the aluminum-silicon alloy, the author based his statement on the solution treatment in the range 500° to 510° C., which is the same as is used for the duralumin-type alloy. The higher soaking temperature employed by Dr. Archer in all probability accounts for the improved physical properties.

J. A. Gann, Midland, Mich.—The question of the stability of magnesium-base alloys is of considerable importance at the present time because of the interest in these alloys in aviation. This was first brought to our attention about 1924. Based on tests then run, we came to the conclusion that there was no change in properties due to aging of magnesium alloys containing aluminum or aluminum plus small amounts of zinc. This week we have rechecked this point on three alloys of which we had duplicate specimens that were not pulled at the time castings were originally made in 1920. The results are as follows:

A 3 per cent. zinc alloy showed an increase of 600 lb. per sq. in. in tensile strength; a 6 per cent. zinc alloy showed an increase of 2400 lb. per sq. in.; an 8.5 per cent. aluminum plus 1.5 per cent. zinc alloy showed an increase of 2300 lb. per sq. in. There has been no appreciable change in hardness in any of these three alloys during this 8-year period, except in the case of 6 per cent. zinc alloy, where we had an increase of 10 points Brinell. These compositions do not correspond exactly to those discussed in the paper, but the results indicate, in confirmation of Lieutenant Lyon's work, that there may be some room-temperature aging effects in certain magnesium-base alloys.

Recently we have examined these three alloys microscopically and could observe no change in structure except possibly in the magnesium-aluminum-zinc alloy, where we thought we saw a very small change due to the precipitation of the magnesium-aluminum compound in the aluminum-rich areas. This point, however, should be further investigated before definite conclusions are drawn, since the alloys were not carefully examined immediately after casting. It is difficult to state whether this aging effect and increase in strength was due entirely to the aluminum, to the zinc, or to a combination of the two.

The first alloy tested by Lieutenant Lyon contained approximately 4.6 per cent. aluminum. It should show no age-hardening because the percentage of aluminum is below that which will be retained in solid solution at room temperature. Both of the magnesium-aluminum-zinc alloys contain zinc in excess of the solubility limit at room temperature and so may show aging effects.

E. A. Anderson, Palmerton, Pa.—According to the equilibrium diagram for the zinc-aluminum system as advanced by Hansen and Gayler, the solubility of zinc and aluminum at the 256° temperature is in the neighborhood of 35 per cent., sloping down indefinitely to about 15 per cent. at room temperature. In all probability the changes occurring in the zinc-aluminum alloys noted in Table 7 are more in the nature of a reprecipitation of zinc than due to a disintegration of the unstable compound in that system.

Equilibrium Relations in Aluminum-magnesium Alloys of High Purity

By E. H. Dix, Jr.* and F. Keller,† New Kensington, Pa.

(New York Meeting, February, 1929)

The use of magnesium as an alloying element in aluminum alloys has been limited, in general, to comparatively small quantities. In duralumin-type, strong aluminum alloys, magnesium is present to the extent of ½ to ¾ per cent. and various grades of Magnalite and the "Y" alloy of the National Physical Laboratory of England contain up to 1½ per cent. In this country small quantities of aluminum alloy sheet containing 4 per cent. magnesium are produced commercially.

All commercial aluminum contains sufficient silicon to convert a portion of the magnesium added to the compound Mg_2Si. It is well known that the solubility of both magnesium and magnesium-silicide decrease with decrease in temperature. It is, therefore, impossible to separate the age-hardening effect of the magnesium-silicide from that of magnesium, except by the use of aluminum of such high purity that the silicon content is negligible. The present paper is the fifth[1,2,3,4] of a series from the laboratories of the Aluminum Co. of America reporting the results of investigations of the equilibrium relations in aluminum-rich alloys made from the high-purity aluminum manufactured by this company.[5]

Previous Investigations

A number of investigations have been made of the constitution of the complete aluminum-magnesium system and several determinations made

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* Metallurgist, Aluminum Co. of America.

† Assistant Metallurgist, Aluminum Co. of America.

[1] E. H. Dix, Jr.: A Note on the Microstructure of Aluminum-iron Alloys of High Purity. *Proc.* Amer. Soc. Test. Mats. (1925) **25**, Pt. 2, 120.

[2] E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans.* (1926) **73**, 560.

[3] E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc.* Inst. Metals Div., A. I. M. E. (1927) 315.

[4] E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 164.

[5] F. C. Frary: Electrolytic Refining of Aluminum. *Trans.* Am. Electrochem. Soc. (1925) **47**, 259.

of the mutual solubility of the metals in the solid state. Grube,[6] who first determined the constitution and the compounds formed, used very small quantities of metal and relied principally on the results of thermal analysis. More recent investigations have shown his work to be inaccurate. The errors were undoubtedly due to the preliminary nature of the investigation, the low purity of the aluminum, and the small quantities of metal used. He did not determine the equilibrium relations in the solid alloys and examined only a few specimens microscopically.

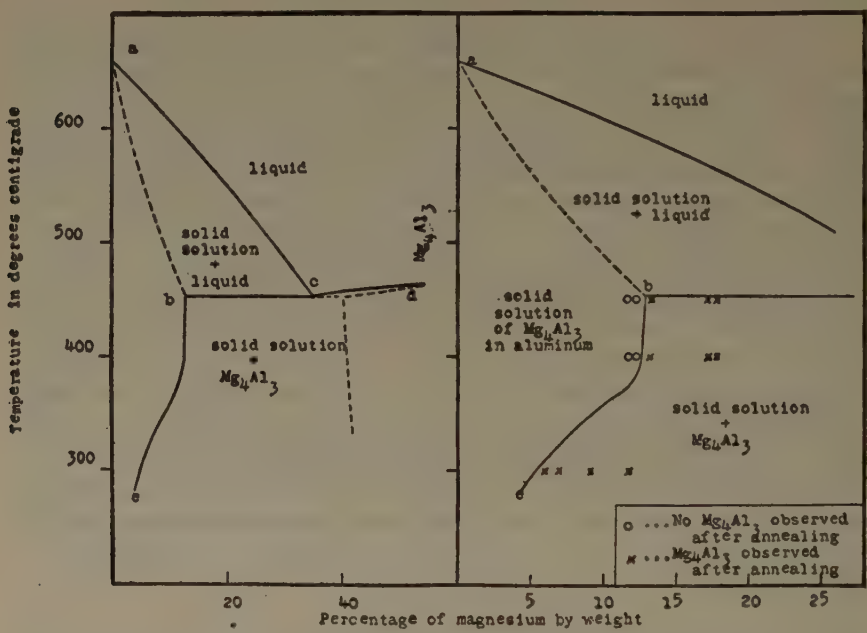

FIG. 1.—DIAGRAM SHOWING ALUMINUM END OF THE ALUMINUM-MAGNESIUM SYSTEM. (MERICA, WALTENBURG AND FREEMAN.)

Merica, Waltenberg and Freeman[7] investigated the solubility of magnesium in aluminum in connection with their work on the hardening of duralumin. Fig. 1 shows the partial diagram published as the result of this investigation. The solid solubility of magnesium is shown to decrease from 12.5 per cent. at 450° C. with decreasing temperature to less than 5.9 per cent. at 300° C.

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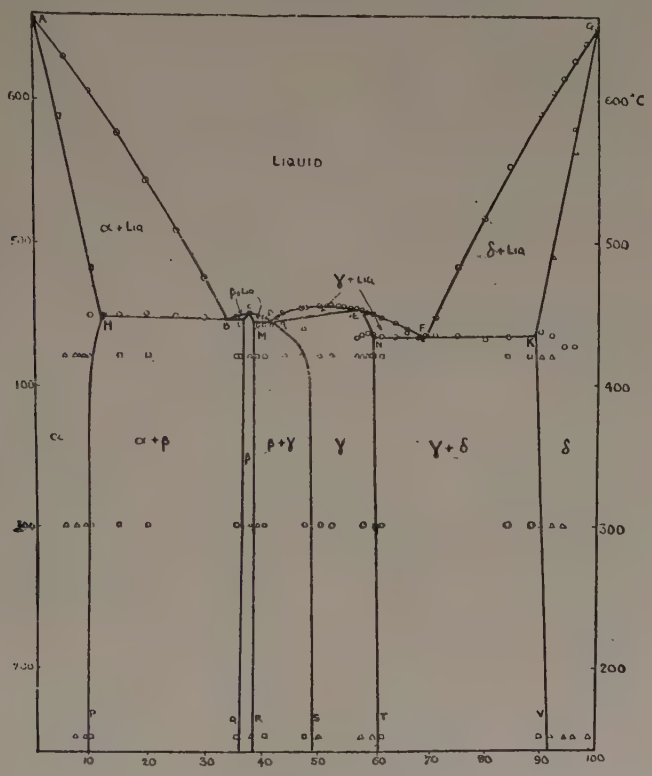
[6] G. Grube: Über Magnesium Aluminiumlegierungen. *Ztsch. f. anorg. Chem.* (1905) **45**, 225.

[7] P. D. Merica, R. G. Waltenberg and J. R. Freeman: Constitution and Metallography of Aluminum and Its Light Alloys with Copper and Magnesium. *Trans.* (1920) **64**, 3, and U. S. Bur. Stds. *Sci. Paper* No. 337 (1919).

Hanson and Gayler[8,9,10] investigated the complete system and published a new diagram (Fig. 2) which has been accepted as more accurate than the one by Grube. The curve of solid solubility differs from the earlier one by Merica and his associates in that the saturation limit at 150° C. is given as 9½ per cent. magnesium.



CONSTITUTION DIAGRAM OF ALUMINUM-MAGNESIUM ALLOYS. (HANSON AND GAYLER.)

Ohtani[11] studied the constitution of alloys containing from 0 to 40 per cent. magnesium, but unfortunately the results of this investigation are available in abstract only. The abstract gives a solubility of 9.7

[8] D. Hanson and M. L. V. Gayler: The Constitution of Alloys of Aluminum and Magnesium. *Jnl.* Inst. Metals (1920) **24,** 201.

[9] D. Hanson and M. L. V. Gayler: The Constitution and Age Hardening of the Alloys of Aluminum with Magnesium and Silicon. *Jnl.* Inst. Metals (1921) **26,** 321.

[10] Eleventh Report to the Alloys Research Committee on Some Alloys of Aluminum, Inst. Mech. Eng. (1921) 218.

[11] B. Ohtani: Alloys of Aluminum and Magnesium. *Jnl. Chem. Ind.* (Japan) (1922) **25,** 36.

per cent. at 400° C. and 7.3 per cent. at 320° C. These results were obtained by using the electrical resistance method.

The Present Investigation

The analysis of the high purity aluminum used in this investigation follows:

Copper, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Aluminum (by Difference) Per Cent.
0.016	0.009	0.020	99.955

The magnesium was obtained from the American Magnesium Corpn. and consisted of the purest extruded, sublimed crystals obtainable.

The following chemical analysis was obtained for this material:

Si, 0.00 per cent.; Cu, 0.00; other group II metals, 0.01; Fe, 0.00; Al, 0.01; Mg(by diff.), 99.98.

Preparation of Alloys

The alloys were melted in a small Hoskins crucible electric furnace, employing crucibles machined from Acheson graphite. A melt of about 500 g. of each alloy was made by melting the aluminum and then adding the required amount of magnesium. For some of the alloys containing more than 10 per cent. magnesium a 20 per cent. magnesium hardener was made and the desired amount of this alloy added to the molten aluminum. The crucible was covered with a graphite lid during melting and extreme care was taken to avoid contamination.

The practice of adding metallic magnesium to molten aluminum appeared to give better castings than when the aluminum-magnesium hardener was used. The use of the hardener caused a greater amount of dross and it was not possible to obtain castings as free from porosity.

The melt was thoroughly stirred, skimmed, and poured into either a cold vertical graphite mold, producing a bar ¾ in. dia. and 3 in. high, or into a horizontal iron mold with an open top, giving a bar ½ in. thick by ⅝ in. high by 9 in. long. The latter type of specimen was nearly free from segregation and porosity and had a very fine structure. There was, however, a slight amount of porosity from piping along the upper surface of these bars, which caused difficulty because of the decomposition of the piped area during annealing. It was necessary, therefore, to remove this part of the specimen before annealing.

Chemical Analyses

The chemical analyses were obtained on drillings from a ⅛-in. thick chill cast plate sample cast from each melt. The chemical analyses and methods of casting the metallographic specimens are given in Table 1.

TABLE 1.—*Aluminum-magnesium Alloys*

No.	Analysis				Method of Casting
	Mg, Per Cent.	Fe, Per Cent.	Cu, Per Cent.	Si, Per Cent.	
1698	3.19				Chill cast in iron mold.
1699	3.68				Chill cast in iron mold.
1696	4.13				Chill cast in iron mold.
1697	4.20	0.03	0.02	0.02	Chill cast in iron mold.
602	4.29				Chill cast in graphite mold.
1725	5.27				Chill cast in iron mold.
656	5.94	0.02		0.02	Chill cast in graphite mold.
695	6.16				Chill cast in graphite mold.
698	6.65				Chill cast in graphite mold.
605	7.40				Chill cast in graphite mold.
604	7.48				Chill cast in graphite mold.
603	8.12				Chill cast in graphite mold.
624	9.44				Chill cast in graphite mold.
657	9.48	0.02		0.02	Chill cast in graphite mold.
625	10.21				Chill cast in graphite mold.
696	11.23				Chill cast in graphite mold.
658	11.79	0.03		0.02	Chill cast in graphite mold.
699	12.06				Chill cast in graphite mold.
697	12.34				Chill cast in graphite mold.
800	13.75				Chill cast in graphite mold.
1621	14.03	0.03	0.02	0.01	Chill cast in iron mold.
801	14.51				Chill cast in graphite mold.
1622	14.97	0.03	0.02	0.01	Chill cast in iron mold.
1726	16.05				Chill cast in iron mold.
802	17.36				Chill cast in graphite mold.
1694	20.52	0.04	0.02	0.03	

Eutectic Temperature

The temperature of the eutectic arrest was ascertained by a number of cooling curves taken on a 200-g. sample of an alloy containing approximately 20 per cent. magnesium. A platinum, platinum-rhodium thermocouple was used in connection with a Leeds & Northrup precision potentiometer and the practice recommended by the Bureau of Standards[12] for protecting the couple from aluminum was followed. The results obtained indicated a eutectic temperature of 451° C., which checked the work of previous investigators.

Annealing Methods

The procedure and apparatus used for annealing to establish equilibrium conditions in the chill-cast alloys have been described in one of the previous papers.[13] The maximum temperature used for annealing

[12] U. S. Bur. Stds. *Tech. Paper* No. 170, 193.

[13] E. H. Dix, Jr. and H. H. Richardson: *Op. cit.*

these alloys was 445° C. The length of time necessary to insure complete equilibrium at this temperature was determined by examining specimens quenched after annealing for 24, 48 and 72 hr. The results indicated that a period of at least 72 hr. was required. A complete history of the six different anneals used in this investigation is given in Table 2. The following is a typical procedure: In order to make certain that equilibrium was obtained the specimens were first annealed at 440 to 445° C. for 168 hr. A group was then rapidly quenched in cold water and the structure taken as representative of equilibrium at this temperature. The balance of the specimens were very slowly cooled at the rate of 25° to 50° in 24 hr. to 400° C. and a group quenched. The remainder were slowly cooled to 375° C., held for 48 hr. and the third group quenched. The temperature was then slowly decreased to 350° C. and held for 72 hr., when a fourth group was quenched and the temperature again lowered to 300° C., held for 96 hr. and the fifth group quenched. The holding time at temperature was increased for each lower temperature because of the greater time required to reach equilibrium at the successively lowered temperatures.

The solubility relations at 200° C. were determined on specimens which had been quenched after 168 hr. at 420° to 435° C. and then reheated at 200° C. in a salt bath for 2 and 4 weeks. The solubility was not determined below 200° C. as the length of time required to establish equilibrium would be too great.

TABLE 2.—*Heat Treatment of Aluminum-magnesium Alloys*

A. Solubility Determinations

First Anneal:

M Nos. 602, 695, 698, 605, 657, 696, 625, 624, 604, 603, 656.

168 hr. at 420° C. and quenched.
168 hr. at 420° C., cooled to 300° C. in 24 hr. and quenched.
168 hr. at 420° C., cooled to 200° C. in 48 hr. and quenched.
168 hr. at 420° C., cooled to 100° C. in 72 hr. and quenched.
168 hr. at 420° C., cooled very slowly to room temperature.

Second Anneal:

M Nos. 658, 699, 697, 800, 801, 802.

168 hr. at 445° C. and quenched.
168 hr. at 445° C., cooled to 400° C. in 24 hr., held 24 hr. and quenched.
168 hr. at 445° C., cooled to 350° C. in 72 hr., held 24 hr. and quenched.
168 hr. at 445° C., cooled to 300° C. in 120 hr., held 48 hr. and quenched.
168 hr. at 445° C., cooled to 150° C. in 192 hr., held 36 hr. and quenched.
168 hr. at 445° C. and slowly cooled in the furnace to room temperature.

Third Anneal:

M Nos. 697, 657, 695, 625, 699, 605, 696, 800, 801, 802, 1622.

168 hr. at 440° C. and quenched.
168 hr. at 440° C., cooled to 400° C. in 24 hr., held 24 hr. and quenched.
168 hr. at 440° C., cooled to 375° C. in 72 hr., held 48 hr. and quenched.
168 hr. at 440° C., cooled to 350° C. in 144 hr., held 72 hr. and quenched.
168 hr. at 440° C., cooled to 325° C. in 240 hr., held 96 hr. and quenched.

TABLE 2.—(*Continued*).

Fourth Anneal:

M Nos. 1 96, 1697, 1698, 1699, 602, 695, 698, 624, 696, 1726.

168 hr. at 435° C. and quenched.

168 hr. at 435° C., cooled to 400° C. in 24 hr., held 24 hr. and quenched.

168 hr. at 435° C., cooled to 375° C. in 72 hr., held 48 hr. and quenched.

168 hr. at 435° C., cooled to 350° C. in 144 hr., held 72 hr. and quenched.

168 hr. at 435° C., cooled to 300° C., in 240 hr., held 96 hr. and quenched.

168 hr. at 435° C., cooled to 225° C. in 360 hr., held 168 hr. at 225° C. and quenched.

Fifth Anneal:

M Nos. 698, 695, 697, 625, 696, 2024, 699, 657, 800, 801, 802, 1621, 1622, 1725, 1726.

168 hr. at 438° C., and quenched.

168 hr. at 438° C., cooled to 400° C. in 24 hr., held 24 hr. and quenched.

168 hr. at 438° C., cooled to 375° C. in 72 hr., held 48 hr. and quenched.

168 hr. at 438° C., cooled to 350° C. in 144 hr., held 72 hr. and quenched.

168 hr. at 438° C., cooled to 315° C. in 240 hr., held 96 hr. and quenched.

The specimens in this anneal were coated with aluminum paint, in an effort to eliminate the blackening of the surface during annealing. The coating of paint did not prevent this effect.

Sixth Anneal:

M Nos. 801, 802, 1621, 1622, 1726.

168 hr. at 440° C. and quenched.

One tube contained the series of specimens packed in the regular manner, while in another tube the specimens were packed in finely divided alumina, in an effort to prevent the blackening of the specimens during annealing. The specimens which had been annealed in the regular manner showed the usual blackened surface, while the specimens which had been packed in alumina showed a bright surface after the treatment.

Reheating:

M Nos. 1696, 1697, 1698, 1699, 602, which had been quenched from 435° C. were reheated in a salt bath at 200° C. for 28 days.

M No. 602, which had been quenched from 420° C. was reheated in a salt bath at 200° C. for 28 days.

M No. 656, annealed 168 hr. at 420° C., slowly cooled to 200° C. and quenched. Reheated 12 days at 300° C. and quenched.

M No. 603, annealed 168 hr. at 420° C. and quenched. Reheated 12 days at 300° C. and quenched.

M No. 604, annealed 168 hr. at 420° C., slowly cooled to 200° C. and quenched. Reheated 12 days at 300° C. and quenched.

M No. 695, annealed 168 hr. at 440° C., slowly cooled to 325° C. and quenched. Reheated 12 days at 300° C. and quenched.

M No. 605, annealed 168 hr. at 440° C., slowly cooled to 325° C. and quenched. Reheated 12 days at 300° C. and quenched.

B. Solidus Determination

M Nos. 800, 1621, 801, 1622, 1726.

72 hr. at 435° C., slowly raised to 452° C., held 20 min. at temperature and quenched.

EFFECT OF ANNEALING

The specimens, after the above annealing treatment, presented a blackened appearance resulting from a decomposition of the surface.

It was found, however, that packing the specimens in tubes with finely divided alumina eliminated this blackening.

Hanson and Gayler state that specimens which had been heated under reduced pressure conditions showed white etching borders on the outside and along cracks which they attributed to a distillation of magnesium. Similar conditions were noted in this investigation in specimens containing a relatively large amount of magnesium when annealed under atmospheric pressure.

It was feared that the distillation of magnesium during annealing might lower the magnesium content to an extent which would affect the accuracy of the solid solubility determinations. For this reason analyses before and after annealing were made on a number of specimens, the compositions of which were near the saturation limit at four annealing temperatures. The entire outer surface of these specimens was removed and the part remaining completely dissolved in sodium hydroxide and analyzed. Some of the differences between the analysis as given by the original plate sample and that of the annealed specimens of the same alloy may have been the result of some slight segregation in the original cast test bars. The analyses of some of the samples after annealing are compared with the original cast analyses in Table 3.

TABLE 3.—*Effect of Annealing on Magnesium Content*

Annealing Temperature, Deg. C.	Cast Analysis; Mg, Per Cent.	Analysis after Annealing; Mg, Per Cent.
350	10.24	10.04
375	11.23	10.68
400	12.06	11.81
440	14.97	14.93

From these results it will be seen that the distillation of magnesium from the specimens during annealing did not appreciably affect the composition of the alloys. The small differences noted, however, were eliminated by plotting the points according to the analysis after annealing.

MICROSTRUCTURE OF THE ALLOYS

Grube[14] showed a maximum on the liquidus curve between 54 and 55 per cent. magnesium, which led him to suggest the formation of the compound Mg_4Al_3. Merica and his associates[15] accepted this formula as representing the constituent found in the aluminum end of the system. However, Hanson and Gayler[16] later submitted their diagram of Fig. 2,

[14] G. Grube: *Op. cit.*

[15] P. D. Merica, R. G. Waltenberg and J. R. Freeman: *Op. cit.*

[16] D. Hanson and M. L. V. Gayler: *Op. cit.*, *Jnl.* Inst. Metals (1920) **24,** 201.

which shows two maxima on the liquidus curve, the first at 37½ per cent. magnesium, corresponding to the formula Mg_2Al_3, and the second at 57 per cent. corresponding to Mg_3Al_2. They state that Mg_2Al_3 and aluminum form a simple eutectiferous series with the eutectic very near the composition of the compound. The temperature of the eutectic arrest is evidently close to the melting point of the compound, thus making it very difficult to determine by means of thermal analyses the constitution in this particular range of composition.

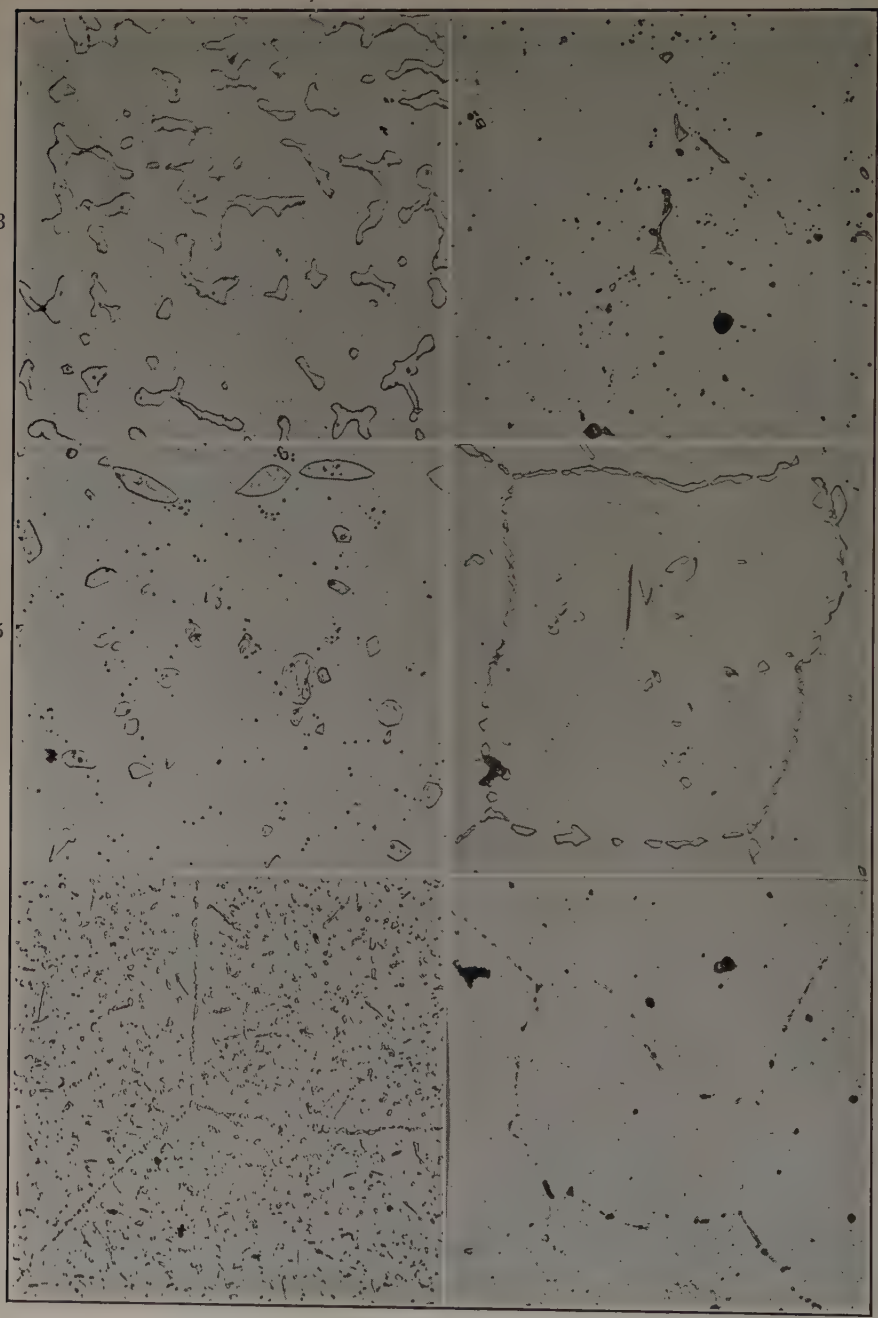
In some unpublished work by J. A. Boyer, in the laboratories of the American Magnesium Corpn. it was found that an alloy containing 37½ per cent. magnesium (the theoretical composition of the compound) when very slowly cooled contained a considerable amount of a second constituent. Increasing the magnesium content above 37½ per cent. increased the quantity of this constituent. Boyer concluded that the constituent occurring in aluminum base alloys had not been identified as a definite compound, but the composition Mg_2Al_3 seemed improbable, and that the constitution is evidently more complex in this region than indicated by the diagram of Hanson and Gayler.

The determination of the constitution in this region is outside of the scope of this paper and in view of the facts presented above the authors prefer to indicate the constituent occurring in aluminum-magnesium alloys containing less than 30 per cent. magnesium, as the β phase.

Fig. 3 illustrates the as cast structure of a rod ½ by ⅝ in. in section of an alloy containing 14.51 per cent. magnesium, cast in an iron mold. This micrograph shows a discontinuous network of β particles in an aluminum-magnesium solid solution matrix. The β constituent is nearly the same color as that of the aluminum matrix and does not polish in relief to the same extent as most of the other constituents found in aluminum alloys. It was found advisable, therefore, to etch the specimens with ½ per cent. aqueous hydrofluoric acid solution in order to bring out the grain boundaries and outline the constituent. This etching solution, which was applied to the polished surface with a soft cotton swab, was very satisfactory in removing small amounts of surface flow.

Fig. 4 illustrates the structure of the same alloy which had been annealed for 168 hr. at 435° C. and quenched. A few particles of β constituent arranged along the grain boundaries indicated that this concentration was just in excess of the solubility limit at this temperature. Fig. 5 shows the amount of excess β constituent formed by slowly cooling the same alloy to 400° C. subsequent to a solution treatment of 168 hr. at 440° C.

Fig. 6 shows a coalesced precipitate of β in an alloy containing 7.40 per cent. magnesium, which had been annealed at 420° C. for 168 hr. and then slowly cooled to 400° C. and quenched, subsequently reheated to 300° C., held for 12 days and quenched. Fig. 7 shows the β precipitate



FIGS. 3–8.—(Captions on opposite page.)

developed by reheating for 28 days at 200° C. an alloy containing 6.16 per cent. magnesium, which had previously been quenched from equilibrium at 400° C. Fig. 8 shows the precipitate of the β phase developed at the grain boundaries by reheating for 28 days at 200° C. an alloy containing 4.29 per cent. magnesium, which had been previously quenched from equilibrium at 420° C. This alloy and the one containing 4.13 per cent. magnesium represented the lowest concentrations of magnesium which showed excess β when in equilibrium at 200° C.

Eutectic Horizontal

The maximum solid solubility and the eutectic temperature were checked by the following experiment:

A series of specimens containing from 14 to 17 per cent. magnesium was annealed for 72 hr. just below the eutectic temperature as previously determined by thermal analysis. After equilibrium had been established by this annealing the temperature was slowly raised to 1° or 2° C. above the eutectic temperature and held for approximately 20 min. and the specimens quenched. The apparatus and method of controlling and accurately ascertaining the temperature of the specimens have been fully described in a previous publication.[17] The specimens treated as described above were examined microscopically for evidence of incipient fusion.

Fig. 9 shows the structure of one of the specimens of this series containing 16.05 per cent. magnesium, which had been subjected to the treatment described above. Incipient fusion at the grain boundaries

[17] E. H. Dix, Jr. and A. C. Heath, Jr.: *Op. cit.*

Fig. 3.—Aluminum alloy (14.51 per cent. Mg) chill cast in iron mold. Etched with 0.5 per cent. HF. × 500.

Shows discontinuous network of β constituent in matrix of aluminum-magnesium solid solution.

Fig. 4.—Aluminum alloy (14.51 per cent. Mg) annealed 168 hr. at 435° C. and quenched. Etched with 0.5 per cent. HF. × 500.

Shows small particles of β constituent remaining after above treatment.

Fig. 5.—Aluminum alloy (14.51 per cent. Mg) annealed 168 hr. at 440° C., slowly cooled to 400° C. and quenched. Etched with 0.5 per cent. HF. × 500.

Shows increase in amount of β constituent over Fig. 4.

Fig. 6.—Aluminum alloy (7.40 per cent. Mg) annealed 168 hr. at 420° C., slowly cooled to 400° C. and quenched; reheated to 300° C., held for 12 days and quenched. Etched with 0.5 per cent. HF. × 500.

Shows coalesced precipitate of β in Al-Mg solid solution.

Fig. 7.—Aluminum alloy (6.16 per cent. Mg) quenched from 400° C. and reheated 28 days at 200° C. Etched with 0.5 per cent. HF. × 500.

Shows coalesced precipitate of β constituent in aluminum-magnesium solid solution.

Fig. 8.—Aluminum alloy (4.29 per cent. Mg) quenched from 420° C. and reheated 28 days at 200° C. Etched with 0.5 per cent. HF. × 500.

Shows precipitate of β constituent at the grain boundaries produced by reheating.

will be observed in this micrograph. A very small amount of incipient fusion was also noted in the alloy containing 14.97 per cent. magnesium, but not in the specimen containing 14.51 per cent. Hence the end of the eutectic horizontal must lie between these two concentrations.

Modified Diagram

The modified solid solubility curve shown in Fig. 10 was based on the results of the microscopic examination of 25 different alloys and six

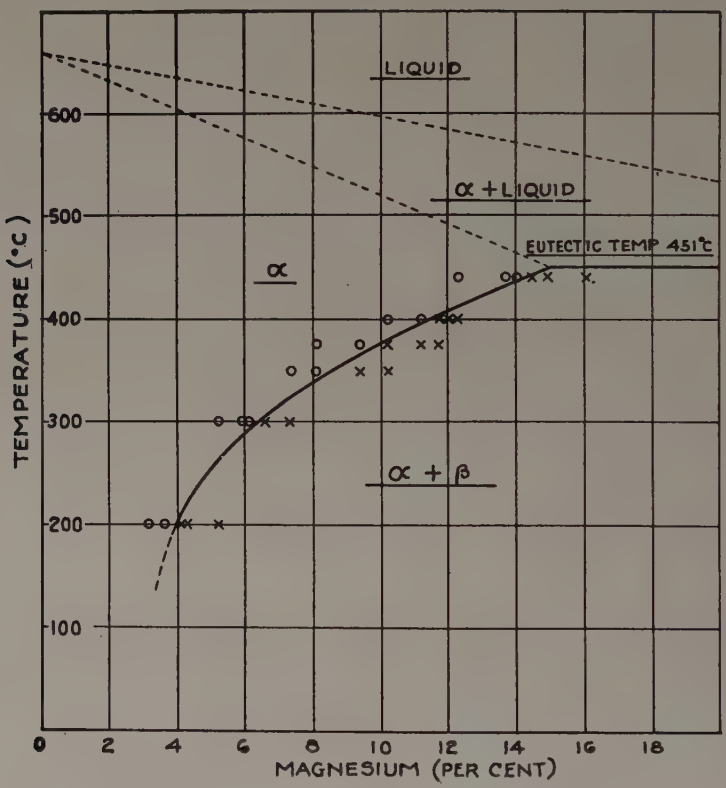


Fig. 10.—Solubility of magnesium in aluminum.

different anneals. The specimens which had been annealed to produce equilibrium at various temperatures were carefully examined in order to detect the presence of even small quantities of β constituent in excess of the solubility limit. In the case of concentrations lying very close to the solubility curve it was at times difficult to determine whether there was any excess constituent present or not, for small, black specks left from polishing could not be differentiated from fine particles of constituent. The fine dots in Figs. 4 and 5 illustrate this difficulty. In such doubtful cases occurring at the lower temperatures the specimens

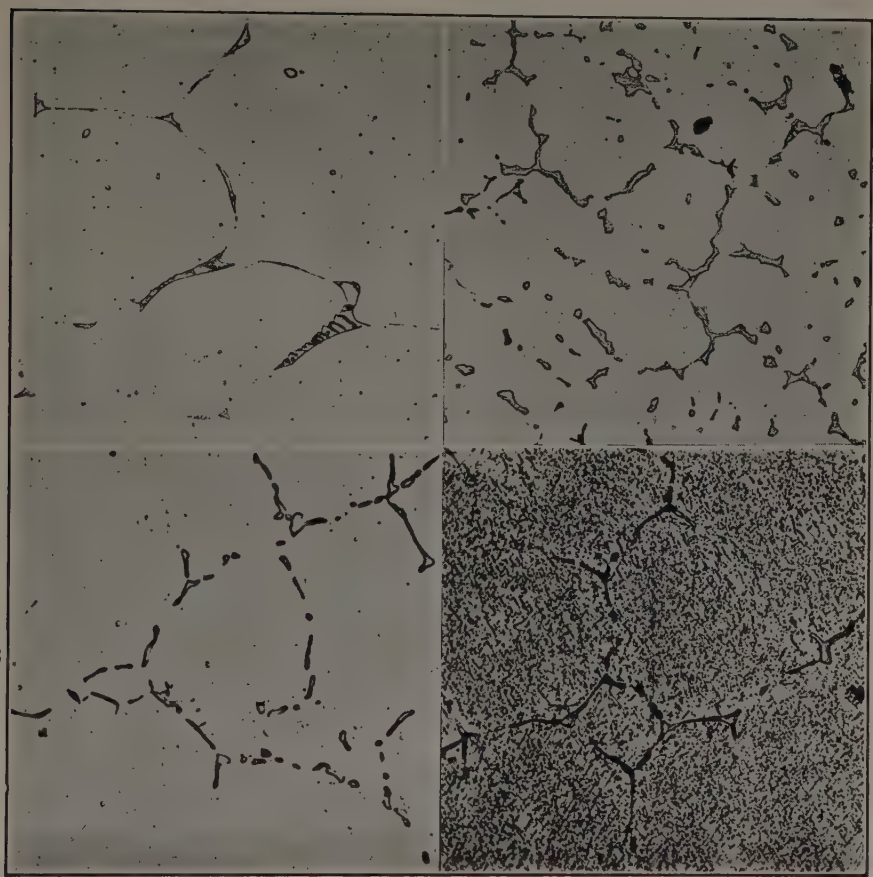


FIG. 9.—ALUMINUM ALLOY (16.05 PER CENT. Mg) ANNEALED 72 hr. AT 435° C., SLOWLY HEATED TO 452° C. AND QUENCHED. ETCHED WITH 0.5 PER CENT. HF. × 500.

Shows incipient fusion of the eutectic.

FIG. 11.—ALUMINUM ALLOY (10 PER CENT. Mg) SAND CAST. ETCHED WITH 0.5 PER CENT. HF. × 100.

Shows network of β constituent.

FIG. 12.—ALUMINUM ALLOY (10 PER CENT. Mg) SAND CAST, ANNEALED 24 HR. AT 425° C. AND QUENCHED. ETCHED WITH 0.5 PER CENT. HF. × 500.

Shows network of insoluble constituent mostly Mg_2Si remaining after the β constituent had gone into solution.

FIG. 13.—ALUMINUM ALLOY (10 PER CENT. Mg) SAND CAST, ANNEALED 24 HR. AT 425° C. AND QUENCHED. AGED 15 HR. AT 200° C. ETCHED WITH 0.5 PER CENT. HF. × 500.

Shows precipitate of β constituent and a network of Mg_2Si.

were reheated a sufficient length of time to cause the particles to coalesce to a size where they could be more readily identified. In any case by comparing such specimens with those of slightly higher magnesium content a very good estimate of the solubility limit could be made.

A modified diagram for the aluminum end of the aluminum-magnesium system, based on the results of this investigation is shown in Fig. 10. The saturation limits for various temperatures are given in Table 4.

TABLE 4.—*Temperature-solubility Relations*

Temperature, deg. C.	451	400	350	300	250	200
Saturation limit (Mg per cent.)	14.9	11.5	8.7	6.4	4.9	4.0

The solubility at the eutectic temperature is thus shown to be less than 2½ per cent. higher than obtained by Merica and his associates and nearly 4 per cent. higher than reported by Hanson and Gayler, while the result obtained at 300° C. substantiates the work of Merica, as opposed to the much higher value of 9½ per cent. reported by Hanson and Gayler. The results which Ohtani obtained by the electrical resistance method are interesting for comparison. At 400° C. his results indicate a saturation limit of 9.7 per cent. which is nearly 2 per cent. lower than that determined by this investigation, although at 320° C. his value of 7.3 is substantiated.

SUSCEPTIBILITY OF ALUMINUM-MAGNESIUM ALLOYS TO PRECIPITATION HEAT TREATMENT

The solubility curve of Fig. 10 shows a difference of approximately 11 per cent. between the saturation limits of magnesium in aluminum at the eutectic temperature and room temperature. This would indicate that these alloys should have great possibilities as regards the susceptibility to precipitation heat treatment. However it has been found to be very difficult to produce satisfactory sand castings from alloys containing 10 per cent. or more magnesium. There is apparently a reaction between the molten alloys and the moist sand which interferes with the production of satisfactory castings. However, the results obtained on test bars, cast to size in sand, of 10 per cent. magnesium-aluminum alloy may be of interest (see Table 5).

TABLE 5.—*Mechanical Properties of Cast 10 Per Cent. Magnesium-aluminum Alloy*

Condition	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness
As cast	20,200	21,610	1.0	71.3
After solution heat treatment	24,300	35,100	8.3	73.0
After solution heat treatment and aging 14 hr. at 150° C.	22,700	34,715	7.3	73.7
After solution treatment and aging 8 hr. at 175° C.	27,825	35,535	5.5	77.7
After solution treatment and aging 12 hr. at 175° C.	28,750	32,925	1.8	87.0

Attempts to improve these properties by artificial aging were unsuccessful. Fourteen hours at 150° C. produced practically no effect, whereas 8 hr. at 175° C. slightly raised the tensile strength and Brinell hardness, but decreased the elongation. Twelve hours at 175° C. caused a marked decrease in tensile strength and elongation, but an increase in Brinell hardness. It is quite possible that a technique of sand casting these alloys could be developed so as to prevent the deterioration previously mentioned, and also that these alloys might hold some promise for permanent mold casting. However, there are other aluminum alloys, notably the aluminum-copper group, which yield just as satisfactory properties and are much easier to handle.

Figs. 11 to 13 are of interest as illustrating the effect of heat-treating on the structure of an alloy of this type. Fig. 11 shows the alloy as sand cast. Fig. 12 shows the same alloy as quenched after a solution treatment of 24 hr. at 425° C. Fig. 13 shows the quenched alloy after an aging treatment of 15 hr. at 200° C. This aging increased the Brinell hardness to approximately 100.

The alloys just discussed were not made from high purity metal and therefore there was sufficient silicon to produce some magnesium silicide. The network in Figs. 12 and 13 consists largely of this constituent.

ACKNOWLEDGMENT

In conclusion the authors desire to acknowledge with thanks the preliminary work of H. H. Richardson on this investigation and the assistance of G. W. Wilcox in the preparation of the micrographs, and also to express appreciation to H. V. Churchill under whose direction the chemical analyses were made, and also to R. L. Templin, under whose supervision the mechanical tests were made.

DISCUSSION

M. G. Corson, Jackson Heights, N. Y.—The diagram in Fig. 10 seems to be rather perfectly established as far as it is based upon microscopic examination of annealed alloys, and the high-grade technique used by Mr. Dix in investigations of this kind certainly leaves nothing to be criticized.

There remain, however, two points which I believe are open to a great deal of doubt. One lies in the absence of certain features which must accompany any binary diagram of the type investigated by Mr. Dix, the second in the justification of the use of microscopic examination alone for the establishing of constitutional diagrams.

Consider an alloy containing 6 per cent. magnesium. According to the present diagram, in which the liquidus and solidus lines were established by other authorities in the past, this alloy will start its crystallization by forming nuclei with about 2 per cent. magnesium while the last drop of the molten mass will contain about 14 per cent. Mg (and probably more, since one hardly can expect the equilibrium to become fully established during the comparatively short period of crystallization).

In cases of this kind a great deal of coring is to be expected, but while I made only a few aluminum-magnesium alloys, I have never been able to develop any coring whatsoever, no matter what method of etching has been used. This is the more strange in the light of my experience with aluminum-copper, aluminum-zinc, aluminum-copper-zinc and aluminum-nickel alloys, all of which showed a well pronounced coring when etched with Vilella's reagent (a mixture of glycerol, hydrofluoric and nitric acid).

Why does this happen with magnesium? The only possible explanation I could suggest lies in an entirely different shape of the solidus line, as presented by Fig. 14.

Here we imagine the solidus line to occupy either the position *ABC* or *ADC*. In the first case its closeness to the liquidus line will prevent any large difference in the composition of the first crystalline nuclei and of the last drops of the melt and consequently no coring will be found. In the second case the chemical difference between the layers of the crystals will increase rather slowly as long as the composition of the melt is represented by a vertical line to the left of the point *D*. Beyond this latter point, the remaining liquid will crystallize mostly in the shape of the secondary constituent and in its presence the chemical attack in etching will concentrate at the phase boundaries, leaving the chemical differences in the alpha phase entirely undeveloped. Again, no coring will be found.

An alloy with say 6 or 5 per cent. magnesium must evidently represent a uniform alpha phase above the transition line as determined by Mr. Dix. In this region the alloy should also be easily workable. It is reasonable to expect that, either on plain annealing of the cast metal or by combining mechanical work and annealing, a well recrystallized structure with sharp grain boundaries should ensue. Mr. Dix does not show a single photomicrograph of such a kind. Nor could I myself ever obtain a good crystalline photomicrograph of an Al-Mg alloy above 2 per cent. magnesium. Is not this feature too queer and entirely out of agreement with everything we know about such alloys as represent solid solutions in one or another thermal region?

Regarding the transition (solubility) line, as determined by Mr. Dix on the basis of a straight microscopic investigation: Systems of this type occurring in other binary alloys are always accompanied by a possibility of a far-reaching dispersion hardening on the application of the usual process of thermal treatment. An alloy of aluminum with copper containing 5 per cent. of the latter will contain probably less than 7 per cent. by weight and 5.5 per cent. by volume of the ultramicroscopically dispersed $CuAl_2$, and still its hardness will increase from 40 Brinell in the quenched to 120 in the heat-aged state—an increase of 200 per cent. On the other hand, an alloy with 10 per cent. Mg ought to contain about 16.5 per cent. by weight and probably

more by volume of the dispersed secondary constituent containing 36 per cent. Mg. One might expect a hardness of 200 Brinell at least for the 73 Brinell in the quenched state, while the actually obtained hardening does not go beyond 14 units Brinell—an increase of only 20 per cent. Why?

On the other hand, a hardness of 73 Brinell is decidedly above anything that could have been expected for a solid-solution alloy with aluminum for its base. The latter metal has a hardness of 16 Brinell only and all our information about other aluminum alloys, in fact about alloys in general, points to the impossibility of increasing the hardness of a metal by more than 150 per cent. by alloying it in such a way as to form a uniform solid solution.

The solubility line obtained by Mr. Dix has only one definite meaning; namely, that to its right any point represents a two-phase state under any given conditions, and that this two-phase structure can be made microscopically visible after a certain period of annealing. On the other hand, it does not prove at all that any point to its left represents a uniform solid solution. Previous investigators located the same

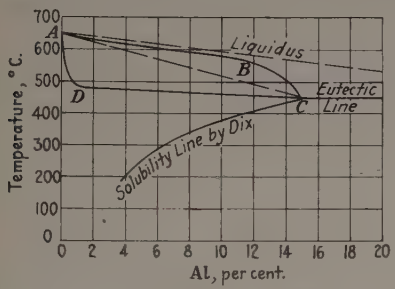


FIG. 14.—POSITIONS OF THE SOLIDUS LINE EXPLAINING THE ABSENCE OF CORING EFFECTS.

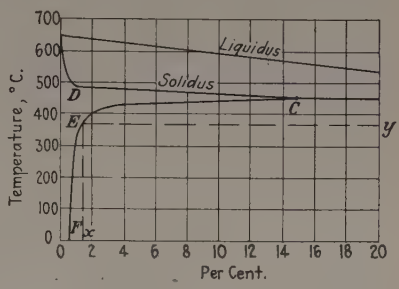


FIG. 15.—HYPOTHETICAL DIAGRAM OF AL-MG ALLOYS.

CEY = region of quick precipitation and rapid growth.
YEX = region of quick precipitation and slow growth.
FEX = region of slow precipitation and slow growth of the beta phase.

solubility line far to the right for the reason that in their experiments the duration of the anneal was too short and the particles of the secondary constituent did not have a chance to grow beyond the ultramicroscopic size. By analogy we can infer that alloys which at the annealing temperatures used by Mr. Dix appeared to lie to the left of the solubility line might also show the secondary constituent if the anneal had lasted 10 times as long.

It is unfortunate that Mr. Dix did not take the trouble to incorporate in his experimental methods, besides his excellent microscopic technique, such important and fruitful ones as the examination of the electric conductivities and of the volumetric changes. Again, aluminum-magnesium alloys of high magnesium content, while they do not hot-roll easily, can be successfully extruded up to 12 per cent. Mg, and constitutional examinations upon wrought alloys are far more instructive than those made upon the cast ones. Work breaks up impurities (oxides), helps to uniformize the chemical composition, helps to obtain a more definite grain formation, etc. An examination of the electric conductivities would locate a precipitation of the secondary phase while its crystals are still far too small to show up at any magnification, and for this reason might have supplemented the visual examination in the most definite manner. It is regrettable that large companies do not make use of all these methods even when they start upon the road of fundamental research, particularly because

there are no scientific institutions that can afford to restudy problems of this kind in a thorough manner, and thereby fill in the gaps.

Mr. Dix and Mr. Keller should be congratulated for a well founded mass of new facts indicating where the solubility line may not lie, but their own equilibrium diagram leaves so much unexplained regarding the behavior of aluminum-magnesium alloys that it can not be even approximately true. Not having any facilities for presenting a diagram based upon experimental data, I feel it still possible to suggest a modification as shown in Fig. 15, which I believe will explain many of the strange features of aluminum-magnesium alloys in a quite plausible manner. My solidus line *ADC* explains why the cast alloys show little or no coring and why the secondary phase starts to crystallize out of the melt even in alloys of which the composition is quite remote from the eutectic line. My solubility (transition) line *CEF* explains a number of things; namely:

1. Alloys and states represented by points above the line *CE* can not be retained intact, no matter how drastic the quenching, for the reason that the solubility/temperature factor $d(\mathrm{Mg})/dT$ is too large. The tendency of beta to precipitate is too strong and on passing the line *CE* a large part of the beta precipitates under any set of conditions. On the other hand the temperature at which this precipitation occurs is so high that a considerable grain growth of the beta takes place. This growth, not sufficient to make the grainlets visible, is sufficient to minimize the hardening effects. Still, while some particles remain at the dimensions favorable for the hardening effect, the latter can not be totally absent. For this reason, the cast alloys of Mr. Dix had the excessive hardness of 71 and could still be hardened to 87 Brinell. Had Mr. Dix used extruded alloys, where dispersion phenomena are likely to be better controlled, he probably would obtain the usual hardness of 120 pertaining to nearly all aluminum alloys hardened by heat treatment.

2. The same position of the *CE* part of the solubility line would explain why it is so difficult to work high-magnesium alloys. The temperature range in which they represent true solid solutions is so narrow that either the alloy contains a molten mass at the grain boundaries or is full of the secondary constituent within its grains, and for this reason too hard and stiff for work.

3. The position of the lower part *EF* of the solubility line would indicate a rather low value for $d(\mathrm{Mg})/dT$ below and to the right of *EF*. For this reason such alloys ought to be expected to precipitate the secondary constituent with an extreme difficulty, to say nothing about the obstacle to growth caused both by the complicatedness of the beta structure and the low mobility of the atoms of magnesium corresponding to the same low values of $d(\mathrm{Mg})/dT$.

My hypothesis increases in probability on the basis of the recent investigations of the Al-Ag system by Hansen, who found conditions practically identical with those proposed in this discussion.

C. S. Smith, Waterbury Conn.—I think it is generally preferable, when determining solubility limits, to quench the samples from a high temperature at which they are homogeneous and then to reanneal them at the desired lower temperature, than to cool (slowly) directly to the low temperature. When working on the copper-silicon diagram[17] I found that the former method gave a much more rapid approach to equilibrium. The reason for this is probably connected with the formation of nuclei; for if the alloys are slowly cooled to a point just below the solubility line, they will be in the metastable range and the possibility of the formation of nuclei will be small. On the other hand, if the specimens are first quenched from a high tempera-

[17] C. S. Smith: The α-phase Boundary of the Copper-silicon System. *Jnl.* Inst. Met. (1928) **40**, 359.

ture and then reheated, nuclei will form during the reheating period and the growth of these to the true solubility limit is a comparatively rapid process.

The formation of nuclei is also considerably hastened if the quenched alloy is cold-worked before reheating. Copper-silicon alloys after quenching and hammering to reduce them about 5 per cent. in thickness will reach equilibrium in about 24 hr. at 600° C., but if they are slowly cooled from 780° to 600° at least 48 hr. is necessary before precipitation is complete.

F. Keller.—Mr. Corson's remarks are interesting. He mentions a submicroscopic solubility range and also the fact that he has not seen coring and grain boundaries developed satisfactorily in aluminum-magnesium alloys.

The present solubility line was determined principally by microscopic examination of small chill-cast specimens which were given a prolonged annealing at the various temperatures to insure equilibrium conditions. Of course, other methods may be used to determine the actual solubility, such as the X-ray method and the electrical resistance method. We do not feel that the X-ray method has been developed sufficiently for the results to be interpreted to within very close limits on solubility work. The electrical resistance method has been used to some extent and some of the results by Ohtani, which we quoted, were obtained by this method. However, the method that is used to determine solubility relations is just one factor and it is felt that the question of obtaining equilibrium conditions is important no matter what method is used.

We do not have any trouble in regard to grain boundaries if we etch correctly for this purpose. The reason grain boundaries were not evident in the photomicrographs shown by slides at the meeting was that in order to develop grain boundaries it is necessary to etch rather severely. In this case, the etching reagent attacks the β phase and we did not feel that it would be satisfactory to have photomicrographs in which the constituent was attacked.

Mr. Smith said that it is generally preferable to quench the samples from a high temperature and then reanneal them at the desired lower temperature, than to cool slowly directly to the low temperature. We have obtained good results from annealing at a high temperature and very slowly cooling to the desired temperature and holding for what we considered a sufficient period of time to insure equilibrium before quenching. Both methods should establish equilibrium if the time of annealing is long enough. It is merely a question from which direction we wish to approach equilibrium.

At the lower temperatures, 200° to 300° C., the results were obtained by reheating specimens previously quenched from higher temperatures. Mr. Smith said that equilibrium may be attained more readily if the quenched alloy is cold-worked before reheating. We have also found this to be true and on some of our present investigations we are carrying out solubility determinations on wrought sheet instead of chill-cast alloys. We find that we can readily get satisfactory equilibrium conditions with much shorter annealing times. In some systems it is impossible to use wrought material. It also requires larger quantities of metal, and equipment that is not always available.

In some of the photomicrographs we showed a number of particles of the β phase about as large as we could identify under the microscope. When the particles became smaller, it was extremely difficult to distinguish the particles of constituent from small polishing defects.

E. H. Dix, Jr. and F. Keller (written discussion).—Mr. Corson's remarks may be taken as a general criticism of the methods used in the laboratories of the Aluminum Company of America in determining the equilibrium relations in aluminum alloys made from high-purity aluminum, therefore the authors desire to reply in somewhat

greater length than would otherwise be justifiable. The procedure employed in the present investigation has been used in the following systems in the order named: Aluminum-iron, aluminum-copper, aluminum-manganese, aluminum-silicon, and aluminum-iron-silicon. Of these the aluminum-copper and the aluminum-silicon systems show an appreciable solubility in the solid state. The solubility curves as obtained by a microscopic examination of chill-cast and annealed specimens in these systems have been checked by electrical resistivity measurements on rolled samples and the agreement between the two methods has been extremely close.

The authors agree with Mr. Corson that it is difficult to get the last traces of an element out of solution and that without sufficiently prolonged annealing treatment the precipitate may be so fine that it can not be seen under the microscope. It is equally true that such small quantities of excess constituent cannot be detected by X-ray methods, at least with the present state of our knowledge.

The interpretation of electrical resistivity data is likewise open to question, for although it is generally assumed that the precipitation of a constituent from solid solution decreases the electrical resistivity, there are indications that in some alloys, under some conditions, if the precipitate is of a certain critical size, the resistivity may even be increased. It is aso probably true that particles of submicroscopic size have a greater effect on the electrical resistivity than microscopically visible particles.

There is so little known about the volumetric changes that may be produced by precipitation and coalescence of the precipitate that it would be unwise to draw conclusions regarding solid solubility from volumetric measurements. Some time in the future this method may be developed so that it will be of use in such investigations, but for the present we must use the tools which have been proved.

The direct method, therefore, is that of microscopic examination. Wherever possible this should be checked by electrical resistivity methods. However, from the evidence obtained in the investigation of the aluminum-copper system the authors believe that a submicroscopic precipitate can be coalesced to a size that is readily visible under the microscope, by prolonged heating at a relatively low temperature, such as 200° C. This is illustrated by Figs. 5*d* and 5*e*, shown in a paper by Dix and Richardson.[18] The precipitate of Fig. 5*e* was produced by annealing the specimen shown in 5*d* for two weeks at 200° C. The specimen of 5*d* was originally quenched after 11 days at 540° C.; it contained 4.05 per cent. copper. It has been the authors' experience that the particles of precipitate in the aluminum-magnesium alloys coalesce much more rapidly than in the aluminum-copper alloys.

In the aluminum-silicon system experiments have been carried out by A. C. Heath, Jr. in these laboratories, in which samples have been heated for from 6 to 9 months at 200° C. and the data obtained by electrical resistivity methods, as well as microscopic, agreed with the original solubility curve obtained by methods similar to those used in the aluminum-magnesium system.

Mr. Corson's discussion concerning the probable shape of the liquidus and solidus lines in the aluminum-magnesium diagram is based on a false premise; namely, that it is not possible to reveal coring and grain boundaries in aluminum-magnesium alloys containing more than 2 per cent. magnesium. Fig. 16 shows the chill-cast structure of an aluminum-magnesium alloy containing 10 per cent. magnesium. Coring is plainly visible, as are also grain boundaries which divide the area shown into three grains. Therefore we do not feel called upon to comment further in regard to the highly hypothetical diagram which he has proposed.

Let us come now to the Brinell hardness data by which Mr. Corson attempts to disprove the solubility limits determined by microscopic examination. In the first

[18] E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans.* A. I. M. E. (1926) **73**, 560.

place, the increase in hardness values which he quotes as being produced by aging a 5 per cent. copper alloy seems to exaggerate the situation somewhat. For instance, to quote from the paper by Dix and Richardson, the Brinell hardness of a 4 per cent. copper-aluminum alloy as slowly cooled during solidification is 39, as chill-cast, 44, whereas the same specimen after slow cooling from equilibrium at 540° C. has a hardness of only 30. By quenching from equilibrium at 540° C. the hardness is increased to 65.

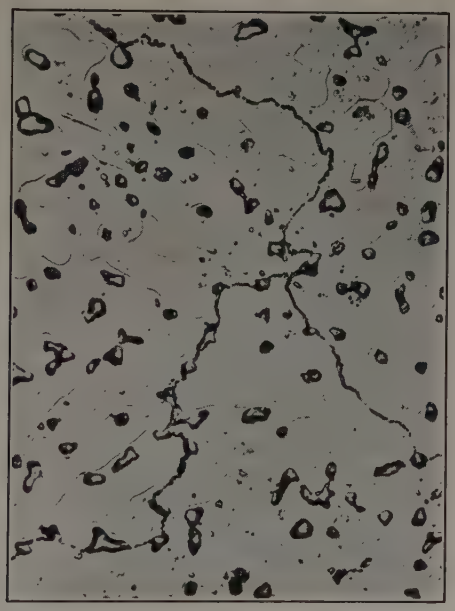


FIG. 16.—ALUMINUM ALLOY (10 PER CENT. MAGNESIUM). CHILL CAST IN IRON MOLD. SHOWS CORED STRUCTURE AND GRAIN BOUNDARIES. × 500. ETCHED WITH HF-HCl-HNO_3.

Archer[19] has given the following values for an alloy containing 4.5 per cent. copper.

Condition	Brinell Hardness
Annealed—large particles of $CuAl_2$	30
Quenched from 540° C.—solid solution	60
Quenched from 540° C.—artificially aged at 150° C., $CuAl_2$ precipitate, very fine particles	110

Thus quenching produces a 100 per cent. increase in hardness over the annealed condition, and aging produces a further increase of about 85 per cent. These figures do not agree very well with Mr. Corson's value of 200 per cent. increase in hardness caused by aging alone. The following Brinell hardness values, which were obtained in the investigation under discussion but not included in the paper, should be of interest, since they substantiate the solubility limits obtained microscopically. They were obtained on an aluminum-magnesium alloy containing 4.29 per cent. magnesium, which had been annealed for one week at 420° C. and then treated in a variety of manners as indicated below:

[19] R. S. Archer: The Hardening of Metals by Dispersed Constituents Precipitated from Solid Solutions. *Trans.* Amer. Soc. for Steel Treat. (1926) **10**, 718.

		Brinell Hardness (10-mm. Ball, 500-kg. Load)
Slowly cooled	Over period of 10 days	45
	To 100° C. and quenched	50
	To 200° C. and quenched	47
	To 300° C. and quenched	46
	Quenched from 420° C	50

The limit of solid solubility at 200° C. as determined by microscopic examination is 4 per cent. The Brinell hardness test is probably not sufficiently sensitive to indicate the effect of the slight amount of magnesium in excess of the solubility limit, but the general trend of these figures indicates that slow cooling, which would tend to throw out the excess compound from solution, gives the softest structure, whereas quenching, which would retain the slight excess of magnesium in solid solution, gives a somewhat harder structure. It is possible that the relatively high hardness shown by the alloy slowly cooled to 100° C. and quenched may be explained by the similarity of this treatment to an aging treatment that would put the small amount of precipitate in condition to produce maximum hardness. Maximum hardness was obtained by aging at 175° C., which is 25° to 50° C. below the temperature at which precipitation would start in an alloy of this composition.

Referring again to Mr. Corson's comments regarding the Brinell hardness quoted in our Table 5: the Brinell hardness of the as-cast alloy containing 10 per cent. magnesium is 71.3. This is a composite value representing the hardness of the aluminum matrix containing an unknown amount of magnesium in solution, plus a network of the hard magnesium-aluminum compound. The tensile strength and elongation of an alloy exhibiting this type of structure are comparatively low. By a solution heat treatment most of the hard network is removed by solution, with the result that there is a marked increase in tensile strength and elongation. There is practically no change in hardness. This indicates that the hardening of the aluminum solid solution by the increased amount of magnesium in solution has just about balanced the effect of removing the hard network of the compound. The aging treatments all tend to lower the elongation with little change in tensile strength and Brinell hardness, except the 12 hr. at 175° C., which treatment reduces the tensile strength and increases the Brinell hardness. This is an indication of overaging. The particles of precipitate have reached a size where they are less effective in strengthening the matrix, but apparently exert the same kind of hardening influence that the network exerts in the as-cast structure.

Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal

By B. Egeberg* and Henry Boynton Smith,* Meriden, Conn.

(Philadelphia Meeting, October, 1928)

Britannia metal is a white alloy consisting primarily of tin and antimony, the tin greatly predominating. The alloy usually contains a small amount of copper and occasionally very small amounts of one or two other metals, such as bismuth, zinc, and lead. It is capable of being cold-rolled, it takes a high polish, and it is fairly noncorrosive; properties which make it a popular metal for many household and traveling utensils. Britannia metal is similar in many respects to pewter and has largely replaced pewter in the arts, but it should not be confused with that alloy, because pewter is essentially a tin-lead alloy, while Britannia is a tin-antimony alloy.

In view of the fact that so little has been published concerning Britannia metal, the authors feel justified in presenting the results of their investigation, particularly since the behavior of this alloy under cold rolling and heat treatment differs so greatly from that of other metals and alloys.

The old craftsman, engaged in the making of ornaments or tableware, heated the cold-rolled sheet metal or his finished product to a straw color corresponding to about 375° F., claiming to produce thereby a harder and more rigid article. The fact that possibly led him to this heating was that a reheated article or sheet made from Britannia metal has a distinct metallic ring when struck a sharp blow, whereas an unheated article or sheet has a leady, dead note. No doubt he has associated the metallic ring with a greater rigidity and strength, and justly so, as will be seen later.

The approximate analysis of the metal we investigated was 91 Sn, 7 Sb, 2 Cu, and the molten metal was bottom-poured into an iron mold yielding an ingot 7¾ in. wide by 11 in. long and ¾ in. thick, the casting temperature being 800° F. The ingot was cold-rolled to a sheet 0.032 in. thick, sufficiently large samples for experimental purposes being cut from the sheet at intermediate stages. The samples were all tested for hardness with scleroscope and Brinell machine, then heated to 212° F. for 30 min., and again tested after cooling to room temperature. The same samples were heated successively at 300°, 400°, and 440° F., followed

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* Metallurgist, International Silver Co.

TABLE 1.—*Tests on Britannia Metals*

	Cold-rolled Condition		After Boiling in Water for 30 Min.		After Heating at 300° F. for 90 Min.		After Heating at 400° F. for 45 Min.		After Heating at 440° F. for 30 Mi.	
	Brinell Hardness	Scleroscope Mag. Hammer	Brinell Hardness	Scleroscope Mag. Hammer	Brinell Hardness	Scleroscope Mag. Hammer	Brinell Hardness	Scleroscope Mag. Hammer	Brinell Hardness	Scleroscope Mag. Hammer
¾-in. cast condition...	23.8	10	22.8	8–9	22.8	9	22.8	7–9	22.8	8–9
Cold-rolled to ⅜ in. in four passes.....	19.7	14	20.1	13–14	19.3	9–10	19.7	9	20.9	8–9
Cold-rolled to ¼ in. in two more passes.....	18.6	14	18.2	13–14	17.8	10–11	20.1	8–9	20.9	9
Cold-rolled to 3/16 in. in one more pass....	17.2	14–15	17.2	14–15	18.6	10–11	20.1	8–9	20.9	8–9
Cold-rolled to ⅛ in. in one more pass.....	15.9	14–15	16.8	14–14½	17.8	11	20.1	9	20.5	8–9
Cold-rolled to 1/16 in. in three more passes..	13.3	15–17	14.8	15–16	17.2	12–13	18.6	10	19.3	10
Cold-rolled to 1/32 in...	Too thin for Brinell	19½–22	Too thin for Brinell	15½–16	Too thin for Brinell	12	Too thin for Brinell	8–9	Too thin for Brinell	

by air-cooling and testing after each treatment. As the melting point was found to be about 460° F., heating was restricted to 440° F. under laboratory conditions and to a temperature of 375° to 400° F. under shop conditions. The results are presented in Table 1.

The furnace used for the experiments was an electrically heated Hoskins laboratory type, chamber size 10 by 4 by 3 in., temperature being recorded by a standardized Leeds & Northrup controller. The samples were slightly raised from the bottom of the furnace, to come in direct contact with the hot point of the thermocouple.

Each scleroscope figure given is the average of at least four readings, and the Brinell figure the average of two impressions, each of which was read in two directions according to standard methods. Further, the figures were all checked upon sheets obtained from the rolling down of an identical ingot cast from a different melt, and the results arrived at were found to agree within limits of experimental error. Lastly, Brinell tests were made using a smaller load (100 kg.) and a 10-mm. ball. The relation between the figures so obtained and those given in the table agree, and therefore are not quoted. In case of the smaller thicknesses two layers of the sheet were used in order to prevent any effect of the anvil upon Brinell results.

Discussion of Results

Considering first the rolled and unheated material in the left-hand column of the table, it will be noticed that the scleroscope hardness gradually increases from 10 to about 20 (when using the magnifying hammer) as the ingot is successively rolled down cold from the ¾-in. size to the finished size of 0.032 inch.

When the same metal was tested with the Brinell machine using a 500-kg. load and a 10-mm. ball, quite contradictory results were obtained, indicating that the metal grew softer and not harder the more it was cold-rolled. The table shows a decrease in Brinell hardness from 23.8 in the cast condition to 13.3 in the rolled sheet 1/16 in. thick. In other words, the two kinds of hardness testing gave entirely opposite results (Fig. 1).

It will be shown later in this paper that the Brinell figures correspond to the strength of the material, and the that Shore instrument is not applicable for judging the physical properties of the metal.

From the columns of the table giving the data after heating the metal at 212° F. (which in this case was obtained by boiling in water for ½ hr.) it will be seen that the hardness of the larger thicknesses was not affected. The sheets 1/16 and ⅛ in. thick—the first mentioned being the smallest thickness we could test accurately with the Brinell machine—have, however, increased in Brinell hardness.

By heating to 300° F. for 1½ hr., a further increase in hardness was developed in the 1/16-in. and ⅛-in. metal, and the next larger size, the

3/16-in., was also affected. The influence on the still larger sizes is so small (probably less than experimental error) that we have not considered it.

By increasing the temperature to 400° F., an additional increase in the hardness of the 1/16-in., the 1/8-in., and the 3/16-in. thick metal was

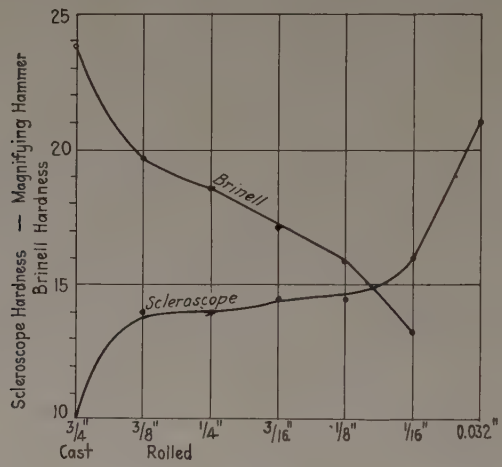

FIG. 1.—BRINELL AND SCLEROSCOPE HARDNESS OF COLD-ROLLED BRITANNIA METAL.

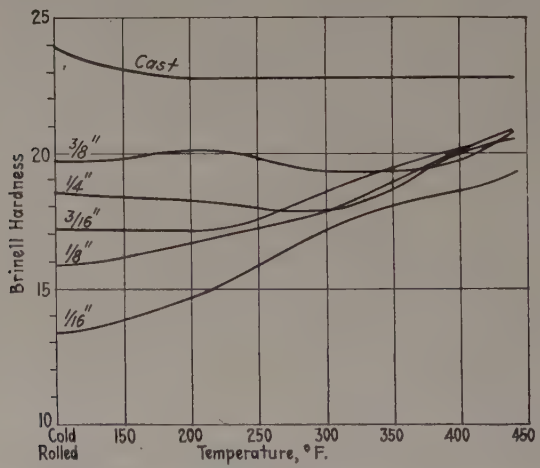

FIG. 2.—CHANGES IN BRINELL HARDNESS OF COLD-ROLLED BRITANNIA METAL DURING HEATING.

observed, and the 1/4-in. size was also affected. Indications are that we have before us an example of depressed recrystallization temperature by increased cold deformation. Only the most deformed crystals recrystallize at the lower temperature, a property that explains the fact that a steady increase in hardness is found within the same sample when it is subjected to a rising temperature. (Fig. 2.)

At 440° F. (20° F. below the melting point) the maximum hardness was obtained, and the effect was extended to the ⅜-in. size. It should be understood, however, that heating to a relatively low temperature for a longer period of time will probably bring about the same effect as heating to a higher temperature for a shorter time. It should also be stated that all samples quoted in the table were air-cooled upon removal from the furnace, and it might therefore be argued that a slower cooling as well as a faster cooling might alter the results. Actual experiments showed, however, that the speed of cooling has but a slight effect on the resulting hardness. For example, a specimen 0.082 in. thick heated to 425° F. for one hour and quenched in water gave a Brinell impression of 3.51 mm. in diameter, while a specimen heated to the same temperature and furnace-cooled gave an impression of 3.56 mm. in diameter. It should be noted that these figures were obtained by using a 100-kg. load and 10-mm. ball.

The data quoted so far have shown that the material becomes softer and weaker the more it is reduced cold in the rolls, and that it becomes harder and stronger the higher it is heated, a temperature just below the melting point having the highest stiffening effect. The actual increase in hardness of the 1/16-in. metal was from 13.3 (as rolled) to 14.8, 17.2, 18.6, 19.3 upon heating to 212°, 300°, 400° and 440° F. respectively. Considering a commercial temperature of 400° F., the increase in hardness would be from 13.3 to 18.6, a 40 per cent. increase, with the possibility of further increase by prolonged heating. Too much attention should not be paid to the accuracy of this figure since the metal becomes softer by cold deforming in the rolls, and it will naturally act the same when cold-deformed by the Brinell ball. By changing the load and the ball in the Brinell machine, a different relation would probably occur. An actual test on blanks heated for 3 hr. at 375° F. and then spun into dishes showed a compression strength of twice the value of a similar dish which was not heated in the blank form.

It is further noted from the table that the rolled metal, even when heated, never regains the hardness and strength of the original cast material. The cast condition seems to be the strongest and the more the reduction, the weaker will be the final product. The cast bar, for example, had a hardness of 23.8. When reduced to 1/16 in. the hardness was 13.3 and after heating at 400° F. it recovered to 18.6, which is still 5.2 points below the cast condition. Comparing the figures for ¼-in. metal in the same manner, the hardness of this size after annealing is only 3.7 points below the cast condition, and thus it becomes apparent that the less the reduction, the harder and stronger will be the metal. It is therefore apparent that Britannia metal should be cast into the thinnest ingot possible when the strength of the rolled metal is a factor of importance.

Considering now the question whether or not the increase in hardness and strength brought about by heat treatment is retained after further cold working, a sheet 3/16 in. thick and one 1/8 in. thick cold-rolled from the same 3/4-in. thick ingot were selected. The sizes mentioned were heated to 375° F. shortly after rolling, whereupon they were reduced in the rolls to 1/16 in. thick in both cases. The results obtained are given in Table 2.

It is apparent that a reduction from 1/8 to 1/16 in., which is considerably more than any blank will receive in spinning or in the press, does not bring about any loss in the hardness and strength obtained by the previous heating. The 3/16-in. however, is affected to some extent upon being reduced to 1/16 inch.

TABLE 2.—*Hardness of Brittania Metal after Heat Treatment and Cold Working*

	Cold-rolled Condition	After Heating at 375° F. for 45 Min.	After Cold Rolling to 1/16 In. Thick	After Heating the 1/16 in. Rolled Sheet at 375° F. for 45 Min.
	Brinell Hardness	Brinell Hardness	Brinell Hardness	Brinell Hardness
1/8-in.	16.5	19.7	19.3	19.3
3/16-in.	17.2	19.7	17.8	18.6

After having been heated, and then rolled to 1/16 in. the two metal sheets referred to were heated again. In the case of the 1/16-in. sheet reduced from 1/8 in., nothing was gained in hardness and strength by this heat treatment, because nothing was lost in the reduction from 1/8 to 1/16 in. In the case of the 1/16-in. sheet reduced from 3/16 in., the metal hardened up somewhat after the final heating, which was to be expected, as a loss took place in the reduction from 3/16 to 1/16 inch.

We believe we have proved that moderate reduction by cold rolling of an annealed metal does not lower to any appreciable extent the physical properties obtained by the heat treatment. This point is important to the craftsman, because it is in many cases impossible to heat the finished article on account of its deformation at moderate heats.

As there might possibly be some difference between the effect of cold rolling and spinning, two blanks were selected of stock 0.038 in. thick. One of these was spun into a shell 9 in. in diameter and the second was spun into an identical shell after it had been heated for 3 hr. at 375° F. Both shells were tested on the rim for compression strength and the load determined that brought about a reduction from 9 to 8 5/8 in. between two diametrically opposite points on the rim. In the first case the load was found to be 713 g. (1.6 lb.) and in the case where the shell was made from a heat-treated blank the load was found to be 1396 g. (3.1 lb.),

thus proving it to be about twice as strong. At the same time this proves that the strength of the metal is in relation to the Brinell hardness and not to the scleroscope hardness.

Conclusions

1. The Brinell test indicates the true hardness and strength of Britannia metal. The scleroscope gives contrary results and the use of this instrument is therefore not recommended for Britannia metal.

2. Britannia metal becomes softer and weaker the more it is reduced by cold rolling.

3. A cold-rolled section becomes continuously harder and stronger upon heating, increasing as the temperature increases up to the melting point (about 460° F.). The hardness of the original cast material is never regained, however, unless subjected possibly to much longer heating periods than those used in this investigation.

4. The ultimate hardness and strength obtained before and after heating depend on the amount of reduction in the rolls. The more the metal is rolled, the weaker it will be, both before and after heat-treating.

5. From 4 it is apparent that the thinner the ingot, the harder will be the metal, because fewer reductions are taken to roll it down to required sizes.

6. The smaller the reduction, the higher is the annealing temperature required to produce a stiffening of the metal.

7. Spun or pressed articles retain the increased hardness and strength brought about by heat treatment of the blank.

8. By making the ingot the thinnest that can be commercially cast, and by heat-treating the cold-rolled sheet at the highest possible temperature without risk of melting, two effective means are at hand whereby the hardness and the stiffness of articles made from Britannia metal can be greatly improved.

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DISCUSSION

O. W. Ellis, Pittsburgh, Pa.—This paper constitutes a valuable addition to our knowledge of the tin-antimony-copper alloys. The effect of plastic deformation on these alloys has, of course, been the subject of experiment before, but the authors have extended the field of research in a direction which, it is really quite surprising, has not been done before.

The authors have shown qualitatively that there is a relationship between the Brinell hardness and the strength of certain of these alloys. They have measured the hardness of these alloys and have also determined the strength of the rims of certain spun articles, but they have not shown whether there is any definite relationship that can be expressed in terms, shall we say, of a simple graph between these two factors, strength and hardness. Such data would be interesting, if they have them available.

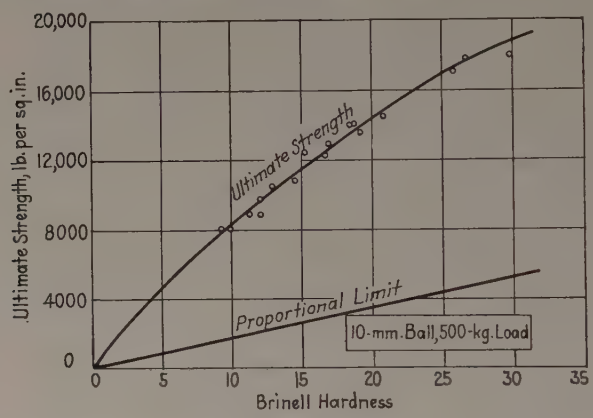

Fig. 3.

Fig. 3 shows the results of work carried out by myself and Mr. Karelitz on a series of these alloys.[1] We found that there was a very definite relationship between the proportional limit of the tin-antimony-copper alloys and their hardness, and also between compressive strength and the hardness.

Fig. 3, the curves in which, however, should not have been extrapolated to the zero point, will show that there is quite a definite relationship between ultimate strength and Brinell hardness, and also between proportional limit and Brinell hardness, for those alloys containing from 0.5 up to 8 per cent. of copper, and from 2 to 10 per cent. of antimony, which were the limits of the compositions that we examined of this system.

The question arises in my mind as to whether any such relationship exists between the hardness and compressive strength of the alloys in various cold-worked and, shall we say, annealed conditions.

Another point that is quite clearly brought out in this paper is that the effect of plastic deformation is to reduce the hardness of a particular alloy of this system. This, of course, is no new discovery. Fry and Rosenhain, to whose work the authors refer in the bibliography, showed that the same was true of an alloy containing 86 per cent. of tin, 8 per cent. of antimony, and 41.5 per cent. of copper. Dr. Greaves, in the discussion of a paper by Thompson and Orme, also presented before the Institute

[1] O. W. Ellis and G. B. Karelitz: A Study of Tin-base Bearing Metals. *Trans.* Amer. Soc. Mech. Engrs. (1928) **MSP 50,** 11.

of Metals in England, showed that the same was true of another alloy of this system. Mr. Karelitz and I have further confirmed this in experiments conducted in the Westinghouse Research Department.

There is a most interesting point that I think has not been emphasized by the authors. They show that on heating cold-rolled Britannia metal, the hardness is increased only if and when a certain fairly definite heating temperature is exceeded, this temperature being lower the greater the amount of deformation. This fact is brought out quite clearly in Fig. 2 of their paper, but is not, I think, referred to in the text.

If that figure is considered carefully, it will be seen that in the case of the alloy reduced 50 per cent. in thickness, no matter to what temperature it is raised after rolling, the hardness remains practically constant. There is a waviness about the hardness-temperature line, nevertheless the hardness may be said to remain practically constant.

In the experiments at East Pittsburgh, we have been concerned with babbitts and therefore were not so much interested in the excessive, if we may call them such, reductions that the authors have used in their experiments. We rolled a number of alloys to 10, 20 and 30 per cent. of their initial thickness as cast and made observations of the hardness of the alloys after rolling, finding that they were reduced in hardness, as the authors and others have found. We measured the hardness also after they had been heated for 1 hr. at 125° C. and we found that the hardness was still further reduced. So it appears that these alloys, if reduced slightly—that is, in amounts of less than 50 per cent.—and then annealed, are still further softened. If they are reduced by about 50 per cent. and then annealed at a series of increasing temperatures, they undergo practically no change at all, but if they are reduced in amounts exceeding 50 per cent., they increase in hardness, if and when a certain definite temperature, which is dependent upon the amount of work that has been put upon them, is exceeded.

The alloys investigated by the authors are supposed to be lead free. I am not clear as to the reason for this. It may, of course, be a matter of color or a matter of tarnishing. In practice with bearing metals, the presence of lead is difficult to avoid. There are, however, many engineers who feel that the presence of lead should be avoided, if possible. Quite a number of statements have been made to the effect that small proportions of lead in tin-base babbitts embrittle the material. We have found that in babbitts containing the tin-antimony compound, additions of lead have a very slight effect, if any, upon the size of the tin-copper needles, but in alloys which contain very small proportions of the tin-antimony compound or no tin-antimony compound at all, the needles, on the substitution of lead for tin, are considerably coarsened. This coarsening of the tin-copper needles may have something to do with the brittleness that has been observed.

Could the authors state whether, in rolling alloys containing lead, if that is ever done, troubles are experienced due to brittleness, and, by so doing, prove or disprove the prevalent ideas regarding the brittleness of tin-base babbitts containing lead?

C. S. Witherell, New York, N. Y. (written discussion).—An interesting feature which the authors of this paper have pointed to is the divergence between the scleroscope and Brinell results. It is generally recognized that the term "hardness" may mean several somewhat different physical properties, or combinations of properties. The scleroscope measures resilience, the Brinell test measures resistance to denting; it is common for the two values (scleroscope and Brinell) to go up and down together; however, it is entirely possible for a material to resist plastic flow and also be lacking in elasticity; heat-treated Britannia metal evidently falls into the latter category.

It is obvious from the authors' work that the Brinell test would be chosen in preference to the scleroscope for manufacturing control in preparing sheet Britannia

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metal, nevertheless the scleroscope results have some meaning; *e. g.*, when such results are low, the material is easily nicked. It certainly is of value to know that the material is not very resilient although reasonably strong.

It appears to me that a scratch test would be of considerable value but not take the place of the Brinell test. Both pewter and Britannia metal surfaces are very susceptible to abrasion, hence any improvement in the scratch-resisting property would be highly desirable. There are two or three recognized scratch tests but probably the most highly developed of all is that described and illustrated by C. H. Bierbaum.[2] Although Mr. Bierbaum's work was primarily on bearing metals, similar tests would be of value for any object wherein the ability to withstand abrasion is important.

The authors are undoubtedly familiar with and have probably made scratch tests. I would like to suggest that they elaborate upon this interesting and valuable paper and give us in the near future results of scratch tests made upon the same or similar samples of cold-rolled Britannia metal.

B. Egeberg.—The scratch tester has not been used by us in this investigation because we have had little success with it in other fields; for example, electroplated silver deposited under various conditions known by practical experience to produce different hardness.

Mr. Ellis remarked that Fig. 2 of our paper contained data not referred

[2] C. H. Bierbaum: A Study of Bearing Metals. *Trans.* (1923) **69**, 972.

Fig. 4.—Structure of Britannia metal cold-rolled to 0.036 in. × 250.

Fig. 5.—Same as Fig. 3. × 750.

Fig. 6.—Specimen from same sheet as Figs. 3 and 4, baked 1 hr. at 400° F. × 250.

Etching solution: 1 part concentrated nitric acid, 3 parts glacial acetic acid and 10 parts of glycerin.

to in the text. Point 6 under "Conclusions" covers what we believe Mr. Ellis has in mind.

For ornamental articles, we have found it advantageous to avoid contamination with lead as far as possible for reason of surface condition. Lead has a tendency to increase the size of the white microconstituent. When the alloy is buffed, it will act in the same way as a journal on a bearing, where there are hard crystals embedded in a soft matrix. The matrix will be dug out and the hard crystals will stand in relief, which is naturally detrimental to the luster desired on ornamental goods.

F. E. Carter, Newark, N. J.—In this paper the rolling drafts were heavy. As I recollect, in the case of copper, if it gets softer on rolling it is due to light drafts being given, and the heavier drafts give the harder metal on rolling. I wonder whether Mr. Egeberg did his rolling with a large number of very light drafts as well as the fewer rather heavy drafts mentioned in the paper, and if so, what were the results.

B. Egeberg.—The number of passes is noted on the table, from which an idea of the reduction in each pass can be obtained.

F. E. Carter.—I observed that, but you would call them heavy drafts.

B. Egeberg.—They are commercial drafts, therefore they are as heavy as possible without causing injury to the metal. We did not experiment with lighter drafts.

B. Egeberg and H. B. Smith (written discussion).—Mr. Ellis says that experiments proved unsuccessful as far as the detection of any elastic or proportional limit of tensile test specimens is concerned. The ultimate tensile strength does not seem to be greatly affected by the original Brinell hardness of the specimen, neither is this to be expected, on account of the great extension and amount of cold work taking place before this point is reached.

The authors propose the following explanation for the abnormal behavior of Britannia metal. Figs. 4 and 5 show the structure of a specimen cold-rolled to 0.036 in. thick. Fig. 6 shows a specimen from the same sheet after having been baked for 1 hr. at 400° F. The disappearance of the white tin-copper constituent after the baking operation indicates that the increase in hardness produced by this operation, as shown by our investigation, is due to the tin-copper constituent being brought into solution by heating and either kept in solution, when subsequently cooled, or precipitated in such a finely dispersed state that it becomes invisible to the microscope. It should be mentioned that the microspecimens have not been prepared by polishing, on account of the great softness of the alloy and its natural tendency to drag and show a distorted surface even when special precautions are taken during polishing. The sheets from which the specimens originate were rolled on a highly polished roll, whereupon the specimens were squeezed against a hardened steel surface which was polished according to regular microscopic routine. In this way satisfactory specimens were obtained with but little expenditure of labor. In case of polishing, operation by hand only could be used with several etchings and repolishings with soap solution before the true structure of the metal developed. This method necessitates a great deal of experience and labor and in the authors' opinion is not as reliable.

High-strength Gold Alloys for Jewelry and Age-hardening Phenomena in Gold Alloys

By E. M. Wise,* Bayonne, N. J.

(Philadelphia Meeting, October, 1928)

The properties required of gold alloys for jewelry are not well standardized, due in part to problems peculiar to certain branches of the jewelry industry, in part to the individual preference of the fabricator and to his willingness to cope with certain difficulties in manufacture, which arise with the use of certain alloys.

General Requirements

In general, the properties desired may be classed as follows:

1. Color should conform to the dictates of good taste and smart style.
2. Corrosion resistance and tarnish resistance should be good. This is to a considerable extent determined by the carat. Resistance to such corrosive agents as mercuric chloride as well as certain depilatories is unreasonable to expect and difficult to meet.
3. Strength and hardness must be adequate to maintain the delicate contours of finely modeled jewelry.
4. Wear resistance must be great enough to resist abnormal wear, such as is encountered by a wedding ring in a lifetime of wear.
5. Ductility must be sufficient to permit the fabrication of drawn shells, tubes and difficult shapes. Material having a yield point of not less than 60,000 lb. per sq. in., an ultimate strength of 100,000 lb. per sq. in., and an elongation of 40 per cent. is desirable.
6. Melting point should be between 800° and 1200° C.

Colored Golds

The popular green and yellow golds are based on the gold-silver-copper alloys; in some cases modified by the introduction of zinc to improve the casting properties and to alter the color, and nickel to increase the strength.

The properties of the Au-Ag-Cu system have been the subject of a very thorough investigation by Jänecke,[1] Sterner-Rainer,[2] and Carter.[3]

* Research Laboratory, The International Nickel Co., Inc.

[1] E. Jänecke: Däs ternäre System Cu-Ag-Au. *Metallurgie* (1911) **8**, 597.

[2] L. Sterner-Rainer: Einige Eigenschaften der Legierungen Au-Ag-Cu. *Ztsch. f. Metallkunde* (1926) **18**, 143, and Rekristallisation und Entfestigung von Edel metallegierungen. *Op. cit.* (1927) **19**, 245.

[3] F. E. Carter: Gold, Silver, Copper Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 786.

Fig. 1 shows the relation between the melting range, ultimate strength, and Brinell hardness for a series of annealed and quenched 14-kt. gold alloys based on the work of Sterner-Rainer. These alloys are of interest in the range from 5 to 12 per cent. Cu, which comprise a series of green golds of various shades; and from about 25 to 41 per cent. covering the yellow and red golds.

The low melting point of these alloys is unfortunate because in other respects their properties are excellent, except perhaps in regard to tarnishing.

The physical properties of a number of modified gold-copper-silver alloys, as determined by the writer, are given in Table 1. As will be

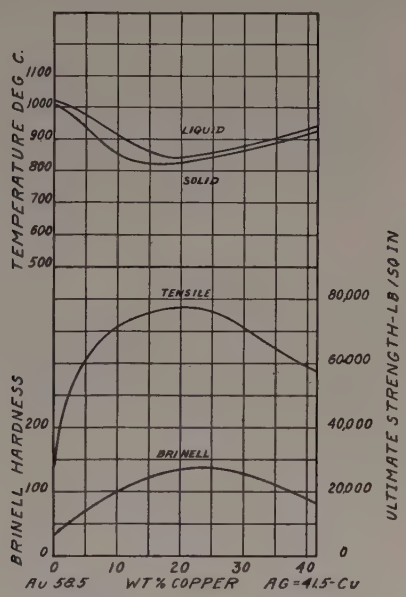


Fig. 1.—Properties of 14-kt. gold-silver-copper alloys.

observed, the strength in the annealed and quenched state ranges between 59,100 and 82,600 lb. per sq. in. and the elongation ranges between 32 and 61 per cent.

Age-hardening

In 1922 the writer made a study of the age-hardening of gold alloys. This was suggested by the work of Merica on the age-hardening of duralumin and bore fruitful results. Table 1 shows that strengths in excess of 100,000 lb. per sq. in. can be developed in all of the alloys listed therein. The great increase in yield point is especially noteworthy. Alloy 1288 shows an increase in yield point from 34,100 to 99,400 lb. per sq. in. on aging at 325° C. for 30 min. The large drop in elonga-

TABLE 1.—*Physical Properties of Colored Gold Alloys*

Alloy Number	Au	Ag	Cu	Ni	Zn	Mn	Other	Per Cent. Elongation in 2 In.	R. A.	Yield Pt., Lb. per Sq. In.	Ult. Str. Lb. per Sq. In.	Treatment				
												Temp., ° C.	Time, Min.	Cooling	Aging, ° C.	Time, Min.
1288 Green	38.5	12.3	31.98	1.84	15.38			61.5		34,100	59,100	700	30	H_2O		
								56.0		47,250	64,000	700	30	Air		
								5.5		99,400	103,000	700	30	H_2O	325	30
								6.0		104,100	108,200	600	30	Air	325	30
1169 Yellow	38.5	15.36	41.86	1.21	3.07			34.0		49,700	83,300	700	30	H_2O		
								28.5		56,100	84,800	700	30	Air		
								26.0		63,000	84,000	600	30	Air		
								6.5		110,500	116,700	700	30	H_2O	325	30
1326 Green	58.35	30.00	6.00	1.5	4.15	0.1		32		52,500	80,400	700	30	H_2O		
								10.5		91,500	104,100	700	30	H_2O	325	30
1293 Yellow	58.35	15.5	25.65			0.50		45		53,300	72,200	750	30	H_2O		
								27		67,500	84,400	750	30	Slowly cooled		
1137 Yellow	58.33	11.03	26.43	2.00	2.21	Tr.		43.5		65,700	82,600	650	30	H_2O		
								50.0		54,200	79,300	700	30	H_2O		
								45.0		57,300	74,800	750	30	H_2O		
								11.5		105,000	110,000	700	30	H_2O	325	30
								10.0		101,800	107,600	750	30	H_2O	325	30
								15.0		99,600	111,100	600	30	Air	325	30
								12.5		102,200	114,000	700	30	Air	325	30

TABLE 2.—*Properties of Gold-nickel Alloys*

Alloys Melted in Acid-lined Crucible

Alloy Number	Atomic, Per Cent.		Weight, Per Cent.		Quenched 700° C.		Phases Present	Quenched 800° C.		Phases Present	Quenched 850° C.		Phases Present	Quenched 900° C.		Phases Present	Furnace Cooled		
	Au	Ni	Au	Ni	K	BHN[a]		K	BHN[a]		K	BHN[a]		K	BHN[a]		K	BHN[a]	Phases Present
3412	90	10	96.8	3.2	−10	63	1	− 7	67	1	− 6	68	1			1	− 9	65	
3413	80	20	93.1	6.9	+23	129	1	+22	126	1	+23	129	1	24	133	1	+22	126	2
3414	70	30	88.7	11.3	+40	213	1	+41	220	1	40	213	1	40	213	1	41	220	2
3415	60	40	83.4	16.6	+43	237	trace 2	47	273	1	46	263	1	45	253	1	41	220	2
3416	50	50	77.1	22.9	+48	284	2			trace 2	49	295	1	49	295	1			2
3417	40	60	69.1	30.9	49	295	2			2	53	347	1	52	333	1			2
3418	30	70	59.0	41.0	53	347	2	49	295	2	55	379	trace 2	54	363	1	38	199	2
3419	20	80	45.6	54.4	48	283	2	46	263	2	51	319	trace 2	51	319	1	38	199	2
3420	10	90	27.2	72.8	36	187	2	33	171	trace 2	34	176	trace 2	34	176	1	35	181	2
Hot-rolled		99									− 4	71	1						

[a] Brinell hardness number.

tion on aging is also of interest, but is not objectionable from a practical standpoint.

The structural changes produced in these alloys by heat treatment are discussed later in this paper.

The Gold-nickel System

This system was for many years considered to be eutectiferous with a limited solid-solution range at each end of the series. Early studies made by the writer on Au-Ni-Zn alloys showed that a large increase in solubility of nickel in gold occurred at high temperatures.

Table 3.—*Properties of Gold-nickel Alloys*

Alloys Melted in Basic-lined Crucible. Carbon 0.01 Per Cent.

Alloy Number	Atomic, Per Cent.		Weight, Per Cent.		Cast		Quenched 870° C.		Furnace Cooled	
	Au	Ni	Au	Ni	K	BHN[a]	K	BHN[a]	K	BHN[a]
60	50	50	77.1	22.9	49.5	300	49	294	34.5	179
126	32	68	61.58	38.42	49.5	300	50.5	313		
131	60	40	83.4	16.6	43.5	240	42.5	231		
132	40	60	69.1	30.9	52	333	50	307		
133	20	80	45.6	54.4	43	236	43	236		

[a] Brinell hardness number.

A series of gold-nickel alloys was made to determine the solid solubility at various temperatures, as well as the hardness and color of the alloys. These alloys contained a small amount of magnesium and were contaminated with a trace of carbon. Hardness determinations were made using the Rockwell diamond cone and a 100-kg. load; the observed values as well as derived Brinell values are given in Tables 2 and 3. The Brinell to Rockwell relations obtained by Petrenko[4] were used:

$$\text{Brinell hardness number} = \frac{768{,}000}{(100 - K)^2}.$$

The solubilities observed are essentially in accord with the recent determinations of Fraenkel and Stern,[5] who have also carefully determined the liquidus and solidus of this system. The thermal data plotted in Fig. 2 are based largely on their determinations with the exception that the melting point of nickel is taken as 1451° C. rather than 1485° C.

The hardness of the alloys oil-quenched from 850° C. rises rapidly with the nickel content until it reaches a maximum of 370 Brinell at 70

[4] S. N. Petrenko: Relationships between the Rockwell and Brinell Numbers. U. S. Bur. Stds. *Tech. Paper* 334 (1927).

[5] W. Fraenkel and A. Stern: *Ztsch. f. anorg. u. allge. Chem.* (1926) **151**, 105 and (1927) **166**, 161.

atomic per cent. nickel; it then falls rapidly to the hardness of pure nickel. The extreme hardness of the 70 atomic per cent. nickel alloys suggests that some precipitation hardening has occurred during the quench although X-ray spectrograms of the quenched alloy show clearly defined diffraction lines, which demonstrates that extensive lattice distortion has not occurred.

By suitably retarding the rate of cooling or by heating to a low temperature, the solid solution existing at high temperatures can be split into a gold-rich and a nickel-rich phase, the composition of the phases being dependent on the aging temperature. The hardness values of a

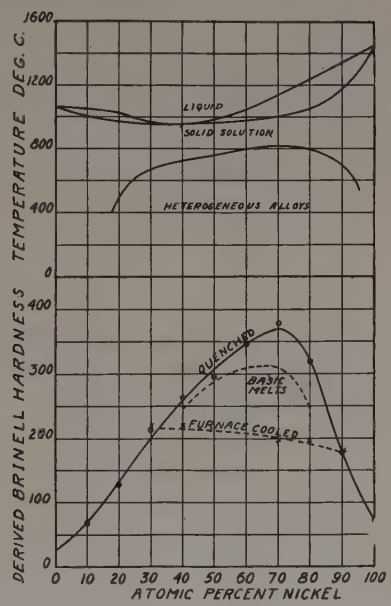


FIG. 2.—PROPERTIES OF GOLD-NICKEL ALLOYS.

series of quenched alloys and of furnace-cooled alloys are shown in Fig. 2. This latter treatment results in a marked decrease in hardness. On slow cooling and aging the 50 atomic per cent. alloy for 15 hr. at 455° C., a further drop in hardness occurs (the hardness in this case being only 86 Rockwell B or 166 Brinell). It might be remarked that a variation in solubility with the temperature seems to be characteristic of gold alloys with Fe, Cr, Ni and Co.

The X-ray structures obtained by Bain for the 50 atomic per cent. gold-nickel alloy, quenched from 860° C. and for the same alloy aged at 455° C., for 15 hr., are shown in Fig. 3. The diffraction pattern of the quenched alloy corresponds to that of a face-centered cubic lattice having a dimension of 3.85 Å. The pattern of the aged alloys shows some

evidence of lattice distortion due to precipitation but gives evidence of the presence of two face-centered cubic lattices having dimensions of 4.00 Å and 3.56 Å, corresponding to gold saturated with nickel and nickel saturated with gold at 455° C. These dimensions would correspond to solutions containing 14.8 atomic per cent. Ni and 3.7 atomic per cent. Au, respectively.

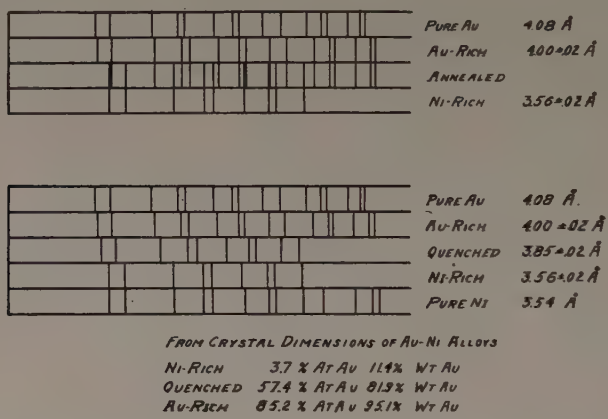
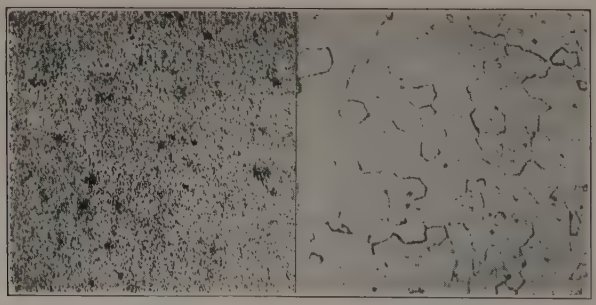


Fig. 3.—X-ray studies of a 50 atomic per cent. gold-nickel alloy.

The microstructures of this alloy in the homogeneous and heterogeneous states are shown in Fig. 4. The structure of the heterogeneous alloy resembles that of a spheroidized high-carbon steel.

The color of the homogeneous nickel golds varies from yellow at the gold end, through a series of unattractive yellowish shades, to a very



Aged Quenched

Fig. 4.—Microstructure of a 50 atomic per cent. gold-nickel alloy. × 100.

pleasing platinum white at 50 atomic per cent. nickel. At higher nickel contents the colors are again unattractive. The colors of the alloys will change in accord with the heat treatment, as would be expected from the equilibrium relations. The 50 atomic per cent. gold nickel becomes dull yellow after protracted aging at low temperatures although the homogeneous alloy is a beautiful platinum white.

The resistance of homogeneous gold-nickel alloys to nitric acid increases with the gold content; passivity being apparent, in the absence of chlorides, at 25 atomic per cent. Au, but in the presence of traces of chlorides the alloys are reactive up to approximately 40 atomic per cent. Au. The slowly cooled gold-nickel alloys are reactive as long as a

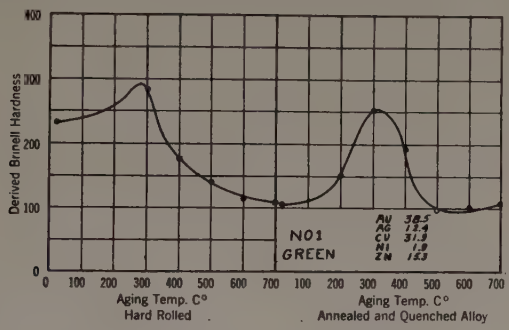


FIG. 5.—HARDNESS CHANGES IN 9.2-KT. GREEN GOLD ALLOY NO. 1 ON ANNEALING AND AGING.

nickel-rich phase is present; *i. e.*, up to about 85 atomic per cent. Au or 95 weight per cent. Au.

WHITE GOLD

The white golds which swept through the jewelry field some years ago were of the Au-Ni-Zn type. When they were first introduced they

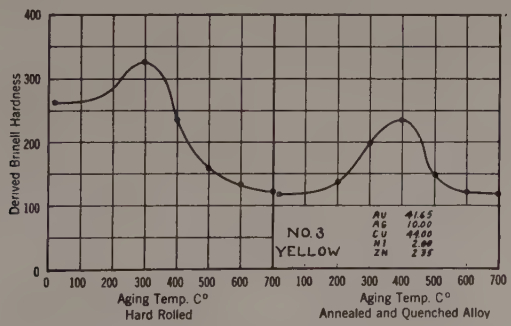


FIG. 6.—HARDNESS CHANGES IN 10-KT. YELLOW GOLD ALLOY NO. 3 ON ANNEALING AND AGING.

gave great difficulty; they would crack on rolling, break in forming and probably crack on annealing. Intensive study largely overcame these troubles, so that it is now possible to secure all forms of jewelry in white golds of good color.

The writer found that very small amounts of copper markedly improved the behavior of the high-carat white golds, the elongation

TABLE 4.—*Properties of White Gold Alloys*

Alloy Number	Au	Ag	Cu	Ni	Zn	Mn	Other	Per Cent. Elongation in 2 In.	R. A.	Yield Pt., Lb. per Sq. In.	Ult. Str., Lb. per Sq. In.	Treatment				
												Temp., ° C.	Time, Min.	Cooling	Aging, ° C.	Time, Min.
1201	37.5		27.59	17.55	17.36			34.0		56,800	105,900	650	30	Air		
White	37.5		27.59	17.55	17.36			35.0		51,100	99,600	750	30	Air		
1214	37.5		25.1	17.4	18.0		1 Sn	34.0		52,100	101,000	700	30	Air		
								34.0		48,300	97,000	750	30	Air		
1209	37.5		25.5	17.4	18.0		1.6 Sn	34.0		51,100	98,400	700	30	Air		
								38.0		50,700	99,000	750	30	Air		
1077	38.5		26.3	22.0	13.0			37.0		59,500	98,600	750	30	Air		
								37.5		59,500	97,700	750	30	Air		
1392	50.0		19.9	20.0	10.0	0.1		42.5		61,100	103,500	750	30	Air		
1390	50.0		21.9	18.0	10.0	0.1		41.0		63,800	105,200	650	30	Air		
								46.0		54,100	95,500	750	30	Air		
1306	58.35		17.95	17.60	6.0	0.1		44.5		68,100	105,100	650	30	Air		
								44.5		64,000	103,000	700	30	Air		
								51.0		58,200	98,300	750	30	Air		
								50		59,400	96,000	750	30	Air		
								58.5		53,800	92,600	800	30	Air		
1361	58.35	0.95	17.00	17.60	6.0	0.1		35		89,600	118,800	650	30	Air		
								49		66,500	101,000	750	30	Air		
1329	58.35		16.95	17.60	7.0	0.15		2		150,000	153,000	None			50 per cent. red.	
								43.5		71,600	108,200	650	30	Air		
								52.5		62,900	99,000	750	30	Air		
								57.0		55,900	94,100	800	30	Air		
								52.5		59,400	95,400	800	30	Air	325	30

1057	58.35		16.0	17.0	8.65			38.0 43.0		67,600 64,500	110,200 105,000	700 750	30 30	Slowly cooled Air		
1057_2	58.35		16.0	16.9	8.65	0.1		41.5 50.0 35.0		62,100 62,000 70,000	102,100 101,500 111,500	750 800 700	30 30 30	Air Air Slowly cooled		
1083	78		2	15	5			34 44	45.7	83,000 76,500	98,100 94,000	750 800	30 30	Air Air		
1088	75		3.5	16.5	5			47 2		82,100 104,000	100,800 109,000	750 750	30 30	Air Furnace cooled		
1086	75		4.0	16	5			35 40.5		86,400 74,900	103,100 94,800	750 800	30 30	Air Air		
1085	76		3.0	16.0	5			41.5 49.0	54.4	86,700 75,900	103,600 94,500	750 800	30 30	Air Air		
1084	77		2.5	15.5	5			33 45	42.8	85,500 78,700	101,300 94,900	750 800	30 30	Air Air		
2	80			14.0	6.0			19.5 29.0	30.6 32.0	81,600	112,400 104,000	650 750	30 30	Air Air		
1	80			16.0	4.0			28.0 28.0	28.0 32.2		115,700 103,200	650 750	30 30	Air Air		
3	80		1	14	5.0			30.5 38.5	31.8 32.8		110,000 103,500	650 750	30 30	Air Air		
2x	80		1	15	4			27.0 43.0		86,500 74,800	110,000 99,500	650 750	30 30	Air Air		

being considerably increased and the tendency to crack on rolling greatly diminished. Pure materials were obtained and a series of white golds of lower carats was then developed which proved very successful.[6] The 14-kt. white, in particular, was very widely used.

The mechanical properties of a number of white golds of various carats are given in Table 4. As will be seen, the mechanical properties

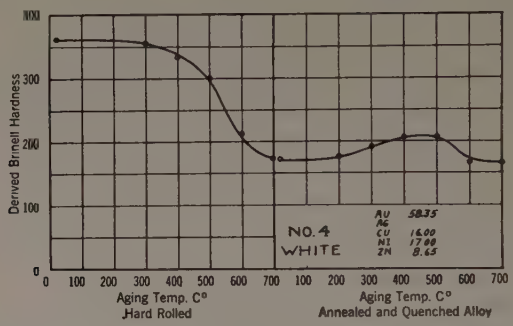


FIG. 7.—HARDNESS CHANGES IN 14-KT. WHITE GOLD ALLOY NO. 4 ON ANNEALING AND AGING.

are excellent, the elongation being usually 40 to 50 per cent. and the ultimate strength of the order of 100,000 lb. per square inch.

The high-carat white gold alloys inherit many of the characteristics of the Au-Ni alloys and are in consequence subject to great changes in

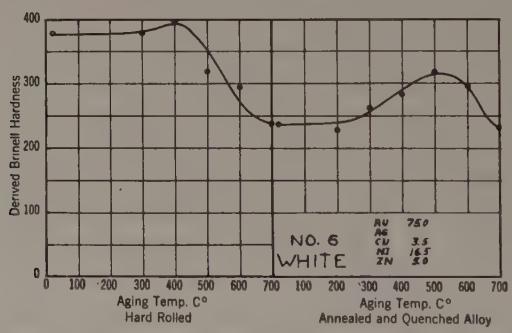


FIG. 8.—HARDNESS CHANGES IN 18-KT. WHITE GOLD ALLOY NO. 6 ON ANNEALING AND AGING.

properties with a variation in cooling rate. A startling example is presented by alloy 1088, which shows an elongation of 47 per cent. when air-cooled but drops to 2 per cent. on furnace-cooling. In general, air-cooling is satisfactory although quenching will produce a slightly softer alloy.

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[6] E. M. Wise: U. S. Pat. 1577995, Mar. 23, 1926.

A fair correlation exists between the color and the hardness in 14-kt. alloys, the whitest alloys being rather hard. The very white alloys, containing 17 per cent. of nickel and from 6 to 8.8 per cent. of zinc, while presenting some difficulty in manufacture, may be successfully fabricated into intricate shapes and drawn into tubes. Where ease of working rather than good color is desired, alloys with a nickel content of 12 per cent. or less may be used. The color of these alloys will range from a slightly red to a greenish tinge depending on the zinc content.

Changes in Hardness and Structure Resulting from Low-temperature Heat Treatment

Marked age-hardening can be produced in a large number of gold alloys, as was indicated earlier in this paper. Four gold alloys, comprising a green gold, a yellow gold and two white golds of various carats, were selected for detailed study. Two sets of samples were prepared, one set being annealed for 1 hr. at 750° C. and oil-quenched; the other set annealed at 750° C. and cold-rolled 50 per cent. Samples of each set were then treated for 1 hr. at temperatures from 200° to 700° C. and oil-quenched.

Hardness determinations were made on all samples after heat treatment, using the Rockwell hardness tester with the diamond cone and a 100-kg. load. These values are designated by K in Tables 5 and 6. Derived Brinell values were obtained by the relation deduced by Petrenko, using the relation Brinell hardness number $= \frac{768{,}000}{(100 - K)^2}$. These derived Brinell numbers are plotted in curves 5 to 8, which show the relation between the hardness and the aging treatment.

The structural changes accompanying the age-hardening phenomena are shown in a series of photomicrographs of these alloys after annealing and aging (Fig. 9).

The great increase in the hardness of the green gold No. 1 on aging for 1 hr. at 300° C., and the yellow gold No. 3 on aging for 1 hr. at 400° C., is of particular interest. If the alloy is cold-worked before aging, the optimum age-hardening temperature is lowered below that obtaining in the annealed and quenched alloy. This is due to the fact that diffusion is accelerated by the lattice distortion resulting from cold work and to the loss of some of the work hardness on reheating.

Little change in microstructure can be observed in alloy No. 3 when aged at 300° C., although considerable hardening has occurred. At 400° C. the presence of a new phase can be observed and the hardness of the alloy is at its peak. At higher temperatures the amount of the second phase increases and the hardness falls. At about 700° C. the alloy again becomes homogeneous and possesses maximum ductility.

The 14-kt. white gold No. 4 shows a considerable increase in hardness on aging at 500° C., coupled with marked changes in microstructure.

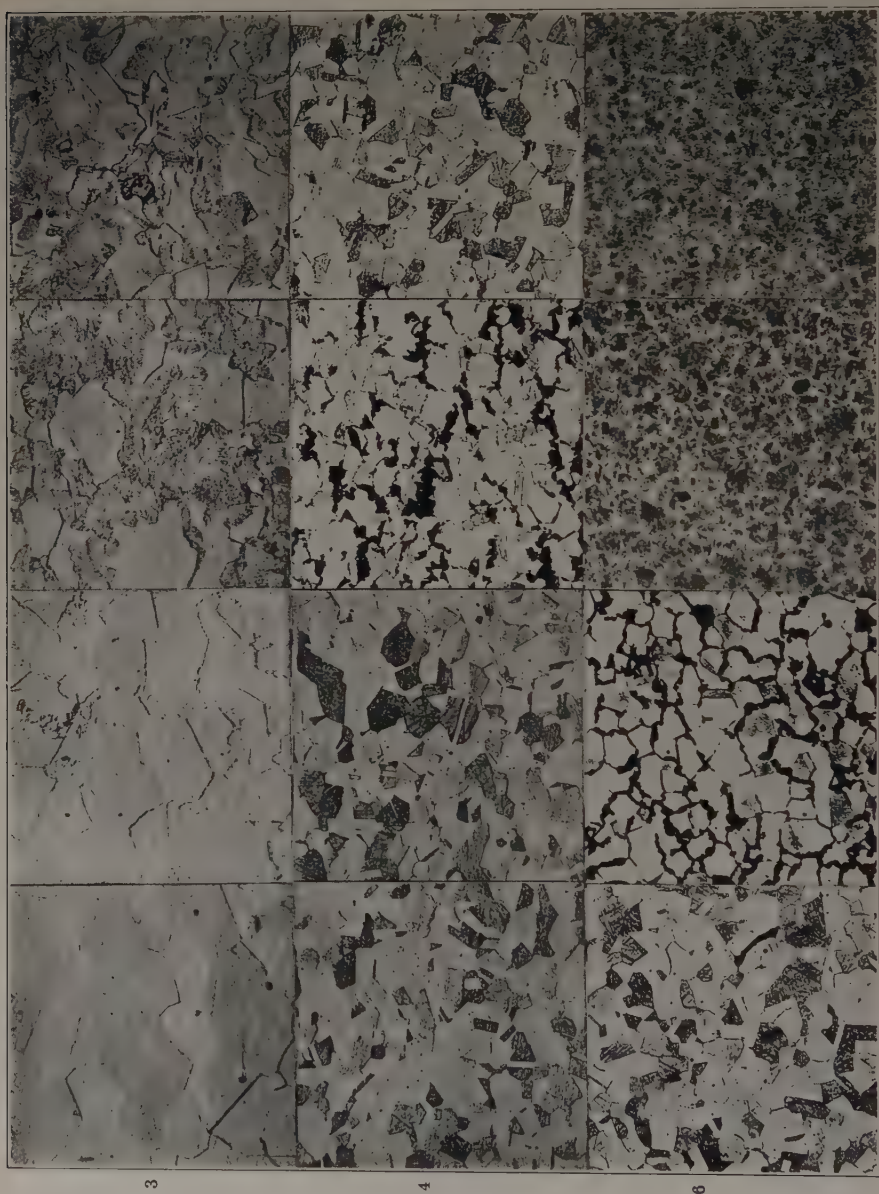

FIG. 9.—MICROSTRUCTURE OF ANNEALED AND AGED GOLD ALLOYS. ×100

Alloy No. 4 shows no precipitation at 400° C. although some hardening has occurred. At 500° C. dark etching regions manifest themselves,

TABLE 5.—*Hardness Changes on Annealing and Aging Gold Alloys*

Alloy Number	Au	Ag	Cu	Ni	Zn	Mn	Initial Hardness		Aged 200° C.		Aged 300° C.		Aged 400° C.		Aged 500° C.		Aged 600° C.		Aged 700° C.		All Treatments 1 Hr. Followed by Oil Quench
							K	BHN[a]	K	BHN[a]	K	BHN[a]	K	BHN[a]	K	BHN[a]	K	BHN[a]	K	BHN[a]	
1 Gr	38.5	12.4	31.9	1.9	15.30		42.5	232			48	283	34	176	26	140	18	114	16	109	Rolled 50 per cent.
							15.0	106	29	152	45	253	37	193	11	97	13	101	15	106	Annealed 750° C.
3 Y	41.65	10.0	44.0	2.0	2.35		46.0	263			51.5	326	43	236	30	157	24	133	20	120	Rolled 50 per cent.
							19.0	117	25	136	37.5	196	43	236	28	148	20	120	19	117	Annealed 750° C.
4 W	58.35		16.0	17.0	8.65	.05	54	362			53.5	355	52	333	49.5	300	40	213	33	171	Rolled 50 per cent.
							33	171	34	176	36.5	190	39	206	39.0	207	32	166	32	166	Annealed 750° C.
6 W	75.0		3.5	16.5	5.0		55.0	379			55	379	56	397	51	319	49	295	43	237	Rolled 50 per cent.
							43.0	236	42	228	46	263	48	283	51	319	49	295	42.5	232	Annealed 750° C.

[a] Brinell hardness number.

TABLE 6.—*Hardness Changes on Cold-rolling Gold Alloys*

Alloy Number	Au	Ag	Cu	Ni	Zn	Mn						
1	38.5	12.4	31.9	1.9	15.3		Red. Per Cent.	0	28	32.5	41.0	48.5
							K	15	37.5	38.0	40.0	42.5
							Brinell	106	196	200	213	232
3	41.65	10.0	44.0	2.0	2.35		Red. Per Cent.	0	9.5	19.8	37.2	49
							K	18	33.0	38.0	43.0	45.5
							Brinell	114	171	200	236	259
4	58.35		16.0	17.0	8.65	0.05	Red. Per Cent.	0	4.4	13.2	29.5	51.5
							K	39	43	47.0	50.5	53.0
							Brinell	206	236	273	313	348
6	75		3.5	16.5	5.0		Red. Per Cent.	0	16.5	29.5	44	49.5
							K	44.0	50.0	52.0	55	55
							Brinell	245	307	333	379	379

originating invariably at the grain boundaries. This precipitate is almost entirely dissolved at 600° C.

The 18-kt. white gold No. 6 shows a marked intercrystalline precipitation at 400° C. At 500° C. the precipitation is general and a bright etching network becomes visible. The presence of the bright etching network is of particular interest and may be ascribed to the increased size of the particles in the region of the original grain boundaries. This is due to the fact that precipitation is initiated at the grain boundaries so that the precipitate in these regions is "older" than the remainder of the precipitate and has in consequence grown to a larger average size. At 600° C. spheroidizing begins and at a slightly higher temperature the alloy becomes homogeneous.

Many of the precipitate structures producible in these alloys present a close analogy with the troostosorbitic structures producible in steels.

These precipitation phenomena in high-carat white golds are not of much interest as a means of increasing their hardness, for that is already adequate, but are of consequence in explaining some of the difficulties encountered in working these alloys, for some of the structures result in an almost total loss of ductility.

It should be pointed out that high-carat white golds aged at 500° C. etch with extreme rapidity, due to the composition and fine state of division of the precipitated phase, a phenomenon readily explained by the peculiar character of the gold-nickel system already discussed.

The change in etching rate with aging temperature is much less marked in the yellow and green golds, as might be expected from their constitution.

Mechanism of Age-hardening of Precious-metal Alloys

The precious-metal alloys offer an interesting array of precipitation-hardening phenomena, involving as they do the precipitation of both compounds and soft solid solutions.

Alloys of gold and copper, palladium and copper and probably platinum and copper as well as gold and zinc, exhibit the formation of submerged compounds which exist over a limited domain of temperature and composition.

Alloys of silver and copper, and gold and nickel, show marked changes in the composition of the two solid solutions existing therein, with the temperature. In the case of silver and copper this change in solubility permits the development of considerable age-hardening, as has been pointed out by the author and others. In the case of the gold-nickel alloys most of the degradation structures are softer than the very hard solid solution.

The presence of small quantities of nickel in certain of these alloys exerts a considerable influence on the age-hardening phenomena either by

entering into some of the compounds mentioned or by reacting with the zinc that is present in the alloy. Nickel or its equivalent, together with the usual compound-forming elements such as tin, silicon and doubtless aluminum or beryllium or the latter alone, may be used to produce hardening but in general their use is not necessary.

The effect of age-hardening on the nobility of the alloy is largely dependent on the nature of the precipitating phase. If the phase formed is high in gold, it will be noble but its formation will involve the withdrawal of some gold from the residual solid solution and to some extent alter its nobility. If the precipitated phase is reactive, as it is in the gold-nickel alloys, very marked changes in the corrosion resistance will occur with certain heat treatments.

In general the age-hardening of precious-metal alloys possesses considerable practical importance, due to the wide range of physical properties attainable by simple heat treatments.

Annealing Cracks

Cracks often develop upon annealing alloys that are in a condition of high internal stress, particularly in material that has been overannealed and then slightly deformed.

White gold alloys are particularly susceptible to this type of failure; due, it is believed, to a slight precipitation of a weak phase at low temperatures. This phenomenon is characteristic of the gold-nickel alloys and is exhibited to a greater or lesser extent by the white golds. The zinc content is also of consequence, the high-zinc alloys giving the most trouble in regard to cracking. Annealing cracks begin to form at temperatures in the vicinity of 250° C. This temperature coincides with the beginning of the precipitation of a second phase, as inferred from hardness changes and electrical resistance measurements. At this temperature the ductility is almost completely lost.

Alloys can be made which show little tendency to fire-crack, but in most cases they have other undesirable features, which render them of only limited importance.

The most effective method for controlling fire-cracking lies in the proper design of the dies or forming tools, and the proper correlation of mechanical operations with the annealing schedule. In dies for shell drawing, it is essential to maintain the proper relation between the reduction in wall thickness and the elongation of the shell, so that excessive residual stresses do not exist in the material prior to annealing. Where possible, 50 per cent. reduction is desirable between anneals, whether the operation involved be cold rolling or shell drawing.

Alloying, Melting, and Annealing

The use of pure metals is of paramount importance; copper in the form of pickled and clipped wire bar is satisfactory. Redistilled zinc is recom-

mended. Nickel low in sulfur, carbon and iron is necessary. The presence of traces of cobalt seems to exert no influence on the alloy. Silver and gold are normally of high purity and need no further comment.

The introduction of small quantities of nickel and zinc is best accomplished by making a base alloy containing copper, zinc and nickel and introducing this alloy into the melt. The direct addition of small quantities of nickel is not recommended.

The high-nickel alloys such as white gold are best made by melting down the complete alloy (Au, Cu, Ni, Zn) under a boric acid flux, stirring well, and then pigging.

A wide variety of deoxidizers and desulfurizers have been tried as additions to gold alloys but most of them serve no useful purpose. Many of these additions, such as Ce, Mg, Ca and Al, spoil the surface of the strip casting and produce an excessive amount of inclusions. Silicon is less harmful in this respect but forms Ni_2Si, if nickel is present, which is only slightly soluble in the presence of large amounts of silver; while even in the absence of silver it retards the grain growth on annealing. Manganese in small quantities can be successfully used but has the somewhat objectionable feature of causing the alloy to become slightly brown on annealing. Phosphorus has been used in certain alloys but increases the hot shortness to an undesirable extent. Zinc, while somewhat ineffective as a deoxidizer, does produce ingots with a good surface. Both lithium and calcium boride present some attractive features and merit consideration.

In general, gas melting is quite satisfactory, although high-frequency melting is feasible and may be used if provision be made for keeping the top of the crucible hot. Melting should be conducted under a heavy boric acid slag, most of the flux being removed when the proper pouring temperature is reached. A little fresh boric acid is then added and a small rod of graphite is introduced which floats on the melt and affords the proper amount of skimming.

The melt is then poured into preheated vertical cast iron molds which have been coated with castor oil. Pouring is conducted slowly and carefully, only sufficient flux being carried over to protect the stream of molten metal from oxidation during the transit from the crucible to the mold. The rate of pouring should be just equal to the rate of solidification in the mold so that little or no pipe will appear in the finished casting. If the pouring rate is too low or unsteady the resulting casting will show cold shuts and should be remelted. The ingot size will be determined by the dimensions of the strip required and by the rolling equipment available. Excessively long ingots are not recommended, as they often cause trouble due to the splashing of metal on to the walls of the mold during the early part of the pour. Where the rolling-mill equipment is adequate,

an ingot about ⅝ in. thick by 2½ in. wide and 10 in. long will be found satisfactory.

The handling of scrap is of importance, for about 60 per cent. of the metal is returned for remelting. Turnings offer special difficulties due to the possibility of mixing various colors of gold and to the possible presence of foreign material such as steel. The large ratio of surface to mass also tends to increase the melting loss. In general, high-carat turnings should be pickled in dilute nitric acid, to remove any base metals that may be present, and then be melted down under a heavy flux and pigged. All light scrap should be melted by starting with a heel of metal in the pot into which the scrap is forced so that rapid melting occurs. Some contamination will take place in spite of these precautions, possibly a slight pick-up of silicon and carbon. It is desirable to introduce some scrap with new melts; in this way all-scrap melts will seldom be necessary.

After casting, the ingots are pickled in hot dilute sulfuric acid to remove the adhering boric acid. In rolling ingots heavy pinches are recommended; light drafts leave high internal stresses in the bar, which will cause splitting on annealing. For the same reason at least 50 per cent. reduction should be made before annealing.

All grease should then be removed from the bar and a protective coating of ocher and boric acid should be applied hot unless a furnace operating under highly reducing conditions is used, in which case no protective coating is required. Gold alloys containing oxidizable metals such as copper show a pronounced tendency to oxidize to a considerable depth on heating under oxidizing conditions producing the so-called "fire." An annealing temperature of 650° C. to 750° C. is satisfactory, the lower temperature being used for the colored golds and the higher temperature for the white golds.

In general, rapid cooling produces the softest metal but some of the alloys, the white golds in particular, are rather tender when hot, so that cracking may result from quenching. The use of hot water for quenching reduces the danger of cracking but many alloys had best be air-cooled to avoid all danger of cracking.

After annealing, the bars are pickled to remove the protective coating and are then washed in hot water and dried. After re-rolling, the strips may be annealed as above indicated or they may be more conveniently handled by a direct electrical annealer, in which case the strips are clamped between two heavy contacts through which is passed a current sufficient to bring the strip to the desired annealing temperature. This arrangement, while not free from objection, is quite satisfactory and is rapid.

Scrupulous care must be exercised to keep the bars and strips clean during rolling operations, to avoid the introduction of small inclusions which remain invisible until the polishing buff discloses them.

Accurate rolling is necessary to secure uniform drawing in press operations and to insure the proper filling of forming dies where little or no possibility exists for taking care of excess metal in the form of a fin or flash. Cross rolling may be necessary to secure sufficiently uniform stock unless very rigid rolling mills are at hand. In general, the thickness should vary less than ± 0.0002 from the standard thickness.

DISCUSSION

R. H. Leach, Bridgeport, Conn.—Mr. Wise speaks of 50 per cent. reduction, but I do not know the exact gages. I wonder if he would be willing to give us the gages, or approximate gages at which those tests were made.

E. M. Wise.—These were cold-rolled from one hundred thousandths to fifty thousandths prior to testing.

T. A. Wright, New York, N. Y.—I congratulate Mr. Wise on his presentation. So far, we in this country have been chiefly indebted to our British and German friends for the attention that they have given to the precious-metal alloys of the gold-silver type, and I think that is in part due to the fact that the jewelry industry in this country has not been so noted for metallurgical progress, as we use the term. What we have done, speaking as a whole, we have been forced to do, with some notable exceptions, one of which is the company with which until recently Mr. Wise has been associated.

There are two or three things of particular interest to me in this, although, considering the amount of work that Mr. Wise has done and the amount that I have been permitted to do, I feel somewhat diffident about speaking on this subject. I think Mr. Wise will agree that, in the main, the efforts of the jewelry industry in work on these metals has been all along the lines of reducing the hardness of the white alloys and increasing the hardness and melting point of the green alloys. For ordinary purposes, in white and not quite so much in yellow we have about all the strength that is ordinarily desired, unless it be in the rather thin, cheap wrist watches that are turned out today. The green gold alloys do not have the strength they should have. In other words, often they will wear like the 22 or 24-kt. alloy.

I was also interested in Mr. Wise's photomicrographs, and I wonder if it is possible (I say this for information and not in criticism) that some of the effects shown might be a matter of the etching reagent. I have not used the solution Mr. Wise has used, and which I think might be brought into the record, but in working in an endeavor to bring out the grain structure of the worked alloys, we have obtained our best results with the use of an electrolytic etch for 2 to 5 sec. in a 5 per cent. potassium cyanide solution. We also found great difficulty in preventing staining. We obtained at times some very weird results, especially in the concentrated solution (Fig. 10). Finally we developed the use of the purest potassium cyanide we could get, because we found in those salts having a fairly high concentration of sodium hydroxide at the beginning we obtained effects which we attributed in part to staining, and in part to protection; in other words, faulty structures, and I should like some comment on that.

For the cast alloys, we found a chromic acid solution with varying amounts of hydrogen peroxide, depending on the solubility of the alloy, brought out the coring and gave practically no stain.

Has it been Mr. Wise's experience that the cracking he has mentioned followed in all cases, or in most cases, the grain boundaries? That has been our experience

(Fig. 11). I recall at the moment an 18-kt. alloy which was being cupped from a 6-in. disk and had reached the stage of a cup 1½ in. dia. and about 1¼ in. high. That sample was mailed in to us. Apparently there were no cracks that could be seen with the naked eye when it was mailed, but when it came to us 24 hr. later it had cracks ⅛ in. wide at the maximum. That could not be attributed to the handling; it seemed as though great stress and strains were set up which were released in that period of time.

In examining that specimen and a number of others, both in the 14 and 18 kt., we found that the cracking invariably followed along the grain boundary, although we could see no occlusions there.

We showed, I think, in the photomicrograph a structure in which there were evidences of recrystallization, but occurring only over a small proportion of the area. I wonder if in that particular case that could be due to the difficulty we have found in

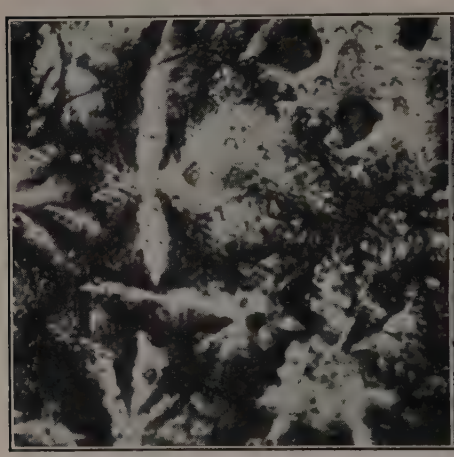

Fig. 10.—14-kt. white gold. × 500. Etchant, 15 per cent. NaOH, 5 per cent. KCN in H_2O. Electrolytic etch, 10 mm. @ 0.15 amp.

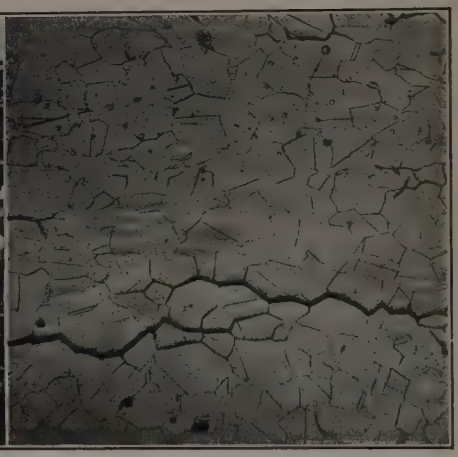

Fig. 11.—18-kt. white gold. × 125. Showing intercrystalline fracture. Etchant, KCN electrolytic.

bringing out and clarifying those grain boundaries without staining. It all had to be done with us along the lines indicated in a very short period of time, and it was important to keep the anode away from the cathode.

E. M. Wise (written discussion).—Mr. Wright is correct in his outline of the present trend of jewelry manufacturers. Heretofore, the softness of the green golds in particular, and to a lesser extent of the yellow golds, was such that fine engraving, barley work and decorations of that kind were rapidly effaced. It has been found possible to greatly improve the wear resistance of these alloys by the age-hardening process. A comparison of the appearance of age-hardened versus untreated finely engraved jewelry after two or three years of wear indicated that a vast improvement in wear resistance had been produced by the age-hardening treatment.

In regard to the hardness of the white golds, apparently there is not much to be done; it is largely dependent on the color desired. With the 14-kt. white gold in particular, we find that as the nickel is increased a certain degree of whiteness is obtained; increasing the copper produces rather a dark shade and perhaps a tendency toward red; increasing the zinc first whitens the alloy but if done with a simultaneous reduction in nickel content results in the production of unattractive greenish shades.

The compositions of the useful white gold alloys occupy a rather limited range and each manufacturer has adopted alloys that fit in with his mechanical processes and possess a marketable color. If a manufacturer is willing to go to a little additional trouble the harder and whiter alloys may be used.

In regard to the etching, we use a mixture of 10 per cent. of ammonium persulfate and 10 per cent. cyanide solutions, except in the case of precipitate structures where the differential etching was very marked and where it is difficult to control the more concentrated solutions. In this case more dilute solutions are better. Many years ago we used the electrolytic etch but finally abandoned it in favor of the cyanide and persulfate solutions. Electrolytic etching is quite effective, but with certain alloys trouble is encountered through the formation of passive films. In the case of alloys containing silver, chlorides cause much trouble. Very peculiar structures may be produced by strong etching solutions applied to the high silver content green and yellow golds.

In all cases of fire or annealing cracking that I have studied the cracks were intercrystalline. I believe that the partial recrystallization noted by Mr. Wright was due to uneven illumination.

The ammonium persulfate and cyanide etch is applicable to a wide range of alloys. Chromic acid is quite effective but I prefer the former combination.

O. W. Ellis, Pittsburgh, Pa.—The gold alloys form interesting systems in that they present certain types of phenomena which are not found in other alloys. In the gold-nickel system, for example, we have conjugate solutions and certain definite temperatures beyond which these conjugate solutions disappear.

Another system that is particularly interesting is the gold-copper system, in which, according to Kurnakow and others, are formed intermetallic compounds at low temperatures from solid solutions. I have used the equilibrium diagram of this system in presenting certain metallographic principles to students and received rather a shock the other day, therefore, to note that there was some question as to whether these two compounds existed at all. My own inquiry is whether the copper auride referred to by Mr. Wise does or does not exist. I should be most sorry to find that this useful diagram, which offers such excellent points for discussion with students, had disappeared.

E. M. Wise.—I am glad that the matter of the presence or absence of the copper auride enters into the discussion. I have no very good evidence of my own, but my opinion is that the AuCu most emphatically does exist. The $AuCu_3$ is under the light of present investigation. Perhaps in the next year or so I may induce Mr. Bain to reinvestigate certain of these alloys to determine the domain of existence of the compound and establish the actual existence of it. In the case of palladium copper, a compound exists which is approximately PdCu, and there is very little question about it. There is precipitation, there is age-hardening, there are all the evidences of the compound formation. In the case of platinum copper, evidence of compound formation is quite apparent and that, too, I hope to investigate in the course of the next year.

C. S. Smith, Waterbury, Conn.—I did some X-ray work on the copper-gold system a few years ago. Unfortunately, it was never possible properly to finish it, but a brief description of some of the results obtained is given in *Mining and Metallurgy* of October, 1928. These experiments showed that the compound CuAu does exist, or at least that there is some phase present in alloys in this range of composition different from the face-centered cubic solid solution. No evidence of the existence of a distinct phase corresponding to the compound Cu_3Au was found. An alloy with 25 atomic per cent. gold, annealed and slowly cooled through the transformation range over a period of five weeks, gave a diffraction pattern consisting of a few lines

due to the compound CuAu superimposed upon the lines due to the undecomposed face-centered cubic solid solution.

E. A. Capillon, Attleboro, Mass. (written discussion).—This paper brings out some interesting facts concerning heat treatment, a subject which apparently has been quite overlooked in the jewelry industry. My experience has been that marked changes can be brought about in the mechanical properties of certain precious-metal alloys by heat treatment. It is unfortunate, however, that in many cases heat treatment involving quenching, although it may greatly improve the working qualities of an alloy, may be unfeasible from the practical standpoint because of serious difficulties caused by quenching cracks. An exception to the preceding statement was found in the case of a white gold solder alloy, containing gold, 41.7 per cent.; silver, 22.4; copper, 13.9; zinc, 15.0 and nickel, 7.0; which could be readily quenched without cracking. An alloy of that composition is at best difficult to roll because of its inherent great hardness. This alloy, however, can be readily reduced 20 per cent. in cross-section in rod-rolling mills if it is previously quenched from 1300° F., whereas in the annealed and slow-cooled condition it will crack when rolled even less than 10 per cent. Hardness measurements on the as-cast alloy gave the following values:

Air-cooled from casting temperature, B 99.1 Rockwell
Reheated to 1300° F. after casting, quenched in water, B 92.9

From photomicrographs it appears that the differences noted are due to the presence of a blue-white dendritic constituent which can be seen in unetched samples of both the slow-cooled and the quenched alloys in both the as-cast and the rolled condition. This constituent is much more extensively distributed in the slow-cooled than in the quenched specimens, apparently on account of lower solubility at room temperature. It is attacked by 20 per cent. nitric acid solution and is apparently a nickel-rich compound or solid solution.

The very marked effect that quenching and aging may produce on the corrosion resistance of an alloy is illustrated by the following data obtained for the binary alloy 75 weight per cent. gold, 25 weight per cent. nickel. Samples of the cast alloy were rolled approximately 50 per cent. and treated as follows:

No. 1. Annealed 1650° F., 1 hr., quenched in cold water
No. 2. Annealed 1300° F., 1 hr., air-cooled

The samples were immersed for 24 hr. in a solution containing 10 per cent. sulfuric acid and 16 per cent. sodium sulfate heated to 160° F. The losses in weight recorded were 0.067 mg. per cu. cm. for sample No. 1 and 0.583 mg. per cu. cm. for sample No. 2, a ratio of about 9 to 1 in corrosion resistance.

F. E. Carter, Newark, N. Y. (written discussion).—This is the first paper we have seen which explains scientifically the cause of the numerous troubles experienced by manufacturers of white golds in the past and which are still encountered occasionally in spite of extensive familiarity with the alloys. Our experiments confirm the author's findings; namely, that gold-nickel alloys are made softer by slow cooling and that white golds (with zinc, etc.) are softened by quenching. Incidentally this tends to show the incompleteness of the explanation that age-hardening is based on the separation of the gold-rich and nickel-rich solid solutions.

As regards age-hardening of gold-silver-copper alloys, it might be inferred from the compositions given in the tables that small amounts of nickel, zinc or manganese might be necessary, and it would seem well to state clearly that gold-silver-copper alloys without any additional elements show the same phenomenon; the effect may be observed in both 14 and 18-kt. golds, the temperature range of age-hardening being particularly wide in the case of the 14-kt. golds.

The practical hints for melting and working will prove useful. We agree that the use of special deoxidizers had best be avoided; and that it is better to depend on the zinc present to deoxidize since a small excess does not have those harmful effects which arise from the use of excessive quantities of other deoxidizers. Bottom-pour graphite crucibles are in our opinion preferable, since a good layer of boric acid flux may be used without any of it getting into the mold.

In melting white golds the pouring temperature is a very important factor, and we find the use of pyrometers almost essential. The pyrometer is enclosed in a graphite tube which acts as a stirring rod for a few minutes prior to pouring; when the millivoltmeter indicates the temperature that experience with the particular alloy has shown to be correct, the pyrometer is removed and the melt promptly poured.

In rolling, the keeping of the sheet flat or nearly flat is of more importance than the amount of the draft; in this connection it might be well to have the author's idea of what constitutes a light and a heavy draft.

E. M. Wise (written discussion).—The studies of Mr. Smith, in conjunction with the work recently published by LeBlanc, Richter and Schiebold[7] fully establishes the existence of the compound CuAu, and the work of the latter group affirms the presence of a special arrangement corresponding to Cu_3Au.

As stated by Mr. Capillon, quenching is not always feasible because of the danger of cracking the alloy. Most alloys transform at a rate sufficiently low so that rather slow quenching media, such as oil, may be used. This reduces the liability of cracking the alloy during the quench.

The change in the hardness of the 10-kt. white gold solder with the variation in cooling rate noted by Mr. Capillon is of interest. Owing to the constriction of the Rockwell scale in the vicinity of 100B, the change in hardness noted (99.1 to 92.9) is of considerable magnitude. The dendritic structure noted in these 10-kt. alloys seems to be typical of the low-carat white gold alloys and can be broken up only with great difficulty.

The influence of heat treatment upon the corrosion rate is indeed striking. Prolonged treatment at temperature below 1300° F. will result in even greater reactivity.

I want to thank Dr. Carter for his contribution and note that his experimental results are, in general, similar to those reported in this paper. The hardness change produced by the precipitation of a second phase in an alloy is not independent of the nature of the precipitated phase. In general, the precipitation of a more or less pure metal produces relatively small hardening. This seems to be true in the case of the precipitation of copper from iron and nickel from gold, the latter being noted on page 399 in the present paper. It should be noted that the precipitation of a copper-rich solid solution from silver does produce appreciable hardening, but greater hardening results from the precipitation of a compound such as $CuAl_2$ from silver, as has been previously pointed out by the writer.

The gold-copper and gold-silver-copper alloys of the proper composition do exhibit age-hardening due to the formation of CuAu, as noted by Dr. Carter, but the presence of other elements, such as nickel, materially increases the hardness of the alloy in most states and probably alters the range of composition of alloys amenable to precipitation hardening. Certain gold-silver-copper alloys, containing considerable zinc, together with a small quantity of nickel, exhibit very marked age-hardening. The hardening constituent has not been identified, but it is improbable that it is CuAu.

My experience with bottom-pouring crucibles is that the ingots poured from such crucibles are slightly rough, due to the oxidation of the metal stream during its

[7] M. LeBlanc, K. Richter and E. Schiebold: Eine Prüfung der Tammannschen Theorie der Resistenzgrenzen am System Gold-Kupfer. Aufstellung neuer Gesichtspunkte. *Ann. physik.* (1928) **86**, 929.

transit from the crucible to the ingot mold. When properly poured from top-pouring crucibles a trace of boric acid will pass over, protecting the metal stream from oxidation. If a reducing atmosphere were maintained within the mold, this objection to the bottom-pouring crucible would be removed.

Pyrometric control of pouring temperature is, as stated by Dr. Carter, quite important.

The reductions used in rolling depend upon a number of factors, such as the diameter, stiffness and surface of the rolls, as well as the power available. In general, a reduction of 15 per cent. per pass would be considered a heavy draft. It is desirable to keep the strip flat during rolling. This may be done by raising or lowering the strip as it enters the rolls. Lowering the strip will usually cause the strip to curve downward on leaving the rolls, although in very hard-rolled materials this effect may be reversed.

Dispersion Hardening in Copper-base and Silver-base Alloys

By J. L. Gregg,* Chicago, Ill.

(New York Meeting, February, 1929)

A study of copper-base and silver-base alloys was made with the object of finding, if possible, useful alloys subject to dispersion hardening. These studies led to the discovery of several alloys showing considerable dispersion hardening, the most important of which, the alloys of copper with iron, nickel, cobalt and chromium silicides, have since been very ably reported by M. G. Corson.[1] This paper is offered as a few notes covering alloys other than those described by Corson and some further data on the silicide alloys.

Copper Alloys

For the purpose of making a rapid survey of copper alloys that might show useful dispersion-hardening phenomena, various alloys were prepared containing 3 per cent. of additional elements added in such proportion that possible compounds could be formed without an excess of either added element. These alloys in the form of rolled or forged pieces were quenched in water from a temperature of 871° C. (1600° F.) and subsequently aged at various lower temperatures for 1-hr. periods. The comparison of the Rockwell hardness of the quenched alloys with the maximum hardness of the alloys after aging was used as a measure of the dispersion hardening.

Table 1 shows the Rockwell "E" hardness (1/8-in. ball, 100-kg. load) of the quenched alloys, together with the maximum hardness resulting from aging. The reheating temperature given in this table is the aging temperature at which maximum hardness resulted from a 1-hr. sojourn. From this table it may be observed that only the silicide alloys showed significant dispersion hardening.

Of these, the only one not described by Corson is the Cu-Be-Si alloy. This alloy contained 1.35 per cent. beryllium and 1.78 per cent. silicon, which is approximately equivalent to 3 per cent. Be_2Si. It had a yellow color and scaled much less than the other silicide alloys upon heating. It could be worked easily either hot or cold but hardened very rapidly on cold working. The annealed alloy upon drawing from a diameter

* Metallurgical Engineer, Western Electric Co.

[1] M. G. Corson: Copper Alloy Systems with Variable Alpha Range and Their Use in the Hardening of Copper. *Proc.* Inst. of Metals Div., A. I. M. E. (1927) 435.

of 0.125 in. to No. 13 gage (0.072 in.) hardened so that it was impractical to draw further with the standard reduction of one B. & S. gage per die. After this amount of drawing, its tensile strength was 158,000 lb. per sq.

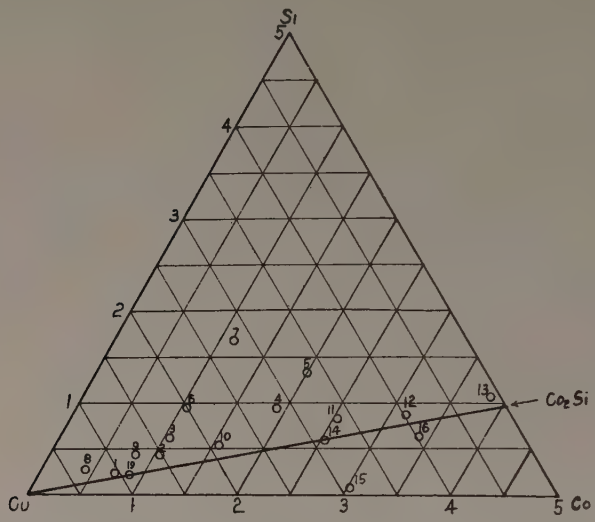

FIG. 1.—COPPER CORNER OF CU-CO-SI DIAGRAM INDICATING COMPOSITION OF ALLOYS INVESTIGATED.

in. After quenching from 871° C., its tensile strength fell to 52,200 lb. per sq. in. and increased to 71,200 lb. per sq. in. when subsequently aged at 427° C.

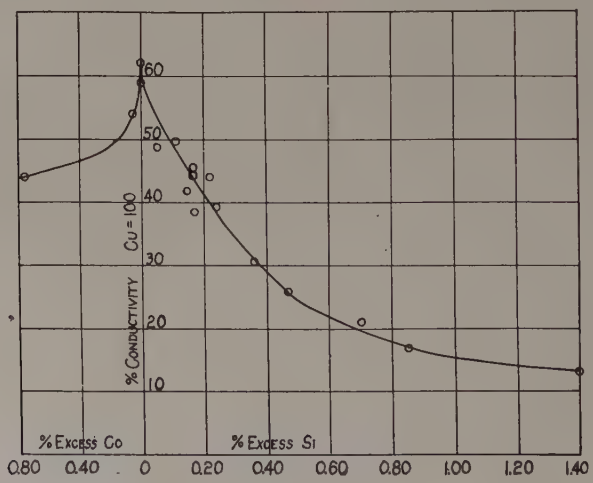

FIG. 2.—ELECTRICAL CONDUCTIVITY OF CU-CO-SI AFTER QUENCHING AND AGING.

As we were desirous of obtaining an alloy of high tensile strength and low electrical resistance, and the cobalt silicides appeared to yield alloys

having the least resistance of the hardenable alloys, the electrical properties of a number of such alloys were determined. The compositions of alloys are illustrated diagrammatically in Fig. 1. The tensile strength and conductivity of these alloys after heat treatment are given in Table 2. Their conductivity in their hardest condition is plotted in Fig. 2 against the amount of excess silicon or cobalt over that required to form the compound Co_2Si *without respect to the amount of* Co_2Si *contained.* The fact that the points fall in two smooth curves, which form a cusp at the ratio of cobalt and silicon necessary to form the compound Co_2Si, furnishes additional proof that dispersion hardening in this instance is due to separation of a definite compound and shows the maximum conductivity that may be expected from hardenable copper-cobalt silicide alloys.

Silver Alloys

The silver alloys listed in Table 3 contained 3 per cent. of added elements, as in the case of the copper alloys, and were quenched from a

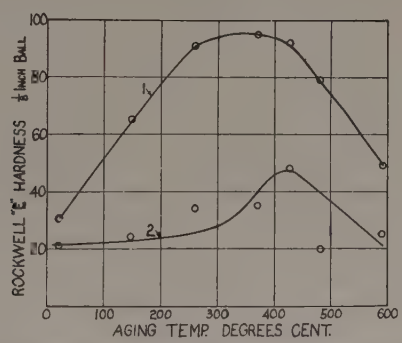

Fig. 3.—Hardness of quenched silver alloys after various aging temperatures.
Curve 1. 3 per cent. $CuAl_2$, 97 per cent. Ag.
Curve 2. 3 per cent. Cu, 97 per cent. Ag.

temperature of 875° C. (1500° F.) and aged at various lower temperatures. Of these alloys only the Ag-Cu-Al alloys indicated marked dispersion hardening. The hardness of the $CuAl_2$ alloy and the Cu alloy are plotted in Fig. 3 against the aging temperature.[2] It is interesting to note that copper aluminide is capable of producing marked hardening in aluminum and nickel, as well as in silver.

[2] W A. Mudge: British Pat. 250194, Mar. 31, 1925.

TABLE 1.—*Hardness of Quenched Copper-base Alloys*

Hardener AB	Solution of A in Base, Per Cent.	Solution of B in Base, Per Cent.	Rockwell "E" Hardness		Maximum Increase in Tensile Strength, Lb. per Sq. In.	Reheating Temperature, Degrees Centigrade
			Quenched	Aged		
Ni_2Si	100	5	50	100	64,000	538
Co_2Si	7	5	55	103	30,000	538
Mn_2Si	100	5	45	73		593
Mg_2Si	0	5	48	53		
Si		5	30	40		
Co		7				
Be_2Si	1	5	69	112	20,000	427
FeSi	3	5	70	88	10,000	
BeNi	1					
$FeAl_3$	3	10	42	65		649
Fe_3Sn	3	14	74	82		649
$FeZn_3$	3	39	30	52		649
Fe		3				
NiA		10	39	48		538
Ni_3Sn_2		14	52	59		593
CoAl	7	10	49	67		649
Co_2Sn	7	14	51	79		649
$CoZn_4$	7	39	21	46		649
Mn_3Al		10	32	46		593
Mn_2Sn		14	44	50		649
Al_2Zn_3	10	39	27	46		593
Ni_3Sn		14	61	62		
Ni_3Sn		14	56	60		593

TABLE 2.—*Properties of Alloys after Heat Treatment*

Number	Cu-Co-Si Wires Quenched from 871° C.		Aged for 1 Hr. at 538° C. after Quenching	
	Conductivity Annealed Copper, Per Cent.	Tensile Strength, Lb. per Sq. In.	Conductivity Annealed Copper, Per Cent.	Tensile Strength, Lb. per Sq. In.
1	23.5	37,600	48.7	72,700
2	18.8	39,100	38.4	79,800
3	18.0	42,750	30.5	71,900
4	16.6	47,500	25.8	72,700
5	13.0	47,500	16.7	67,300
6	14.9	48,800	20.9	72,000
7	11.4	50,000	13.3	73,000
8	26.5	35,600	44.2	56,000
9	21.2	39,900	38.2	73,200
10	21.2	45,300	45.3	76,700
11	20.6	47,800	44.0	75,000
12	20.4	49,700	49.6	79,000
13	20.0	49,600	41.7	69,000
14	20.6	47,500	53.8	79,000
15	14.3	43,500	40.7	52,700
16	18.5	46,500	44.3	58,400
19			59.0	72,250

TABLE 3.—*Hardness of Quenched Silver-base Alloys*

Hardener AB	Solution of A in Base,[a] Per Cent.	Solution of B in Base,[a] Per Cent.	Rockwell "E" Hardness		Reheating Temperature Degrees Centigrade
			Quenched	Aged	
$CuAl_2$	6	4	30	95	371
Cu_2Mg	6	28	4	40	427
Cu_2Sb	6	16	10	33	150
$MgZn_2$	28	204	2	38	427
Cu_2Cd_3	6	32	−2	7	371
CdSb	32	10	−3	20	371

[1] Most of these solubilities are taken from Guertler: *Ztsch. f. Metallkunde* (1927) **19**, 68.

The Constitution of the Copper-silicon System

By Cyril Stanley Smith,* Waterbury, Conn.

(Philadelphia Meeting, October, 1928)

Isolated alloys of copper and silicon were prepared and examined by chemical methods more than one hundred years ago, but it was not until the work of Rudolfi[1] that the equilibrium relations were studied. The early history of the alloys was well described by Baraduc-Muller[2]

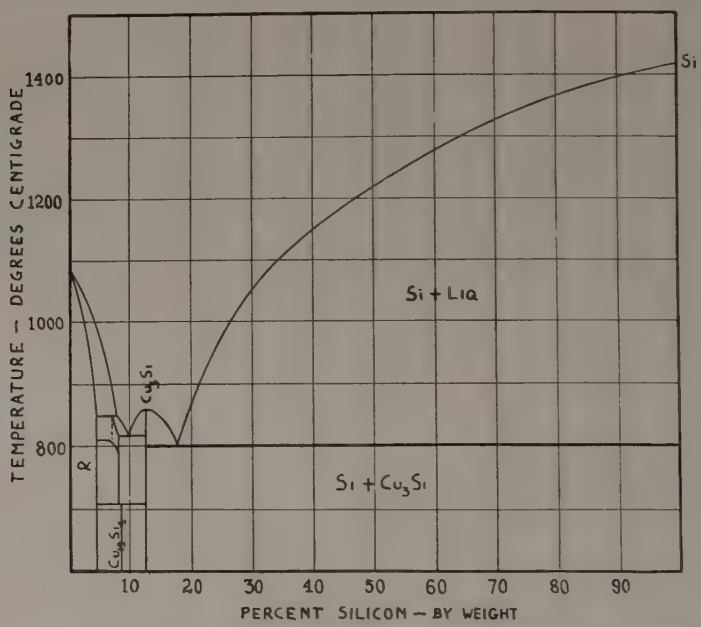

Fig. 1.—Copper-silicon equilibrium diagram according to Rudolfi (1907).

and need not be further discussed here. The diagram of Rudolfi, based entirely on thermal observations, showed silicon to be soluble in copper up to 4.5 per cent. at 849° C., at which temperature there was a peritectic horizontal resulting from the formation of a β phase with about 7.4 per cent. silicon from α and liquid with 7.85 per cent. silicon. The β phase was believed to form a eutectic with Cu_3Si at 820° C. and 9.8 per

* Research Laboratory, American Brass Co.

[1] E. Rudolfi: Die Silicide des Kupfers. *Ztsch. anorg. chem.* (1907) **53**, 216.

[2] L. Baraduc-Muller: Action de carbure de silicium sur quelques oxydes metalliques. *Rev. Met.* (1910) **7**, 711.

cent. silicon. It was supposed to undergo a continuous change in composition on cooling between 810° and 780° C., and to decompose at 710° into $Cu_{19}Si_4$. The phase Cu_3Si was shown to form a second eutectic with pure silicon, at 17.6 per cent. silicon and 800° C. No investigators other than Rudolfi have determined the diagram in the range above 20 per cent. silicon, and for this reason, as well as for comparison with the newer work on the copper-rich alloys, his diagram is reproduced in Fig. 1.

The most complete and accurate work which has hitherto been published is that of Sanfourche,[3] whose diagram is reproduced in Fig. 2.

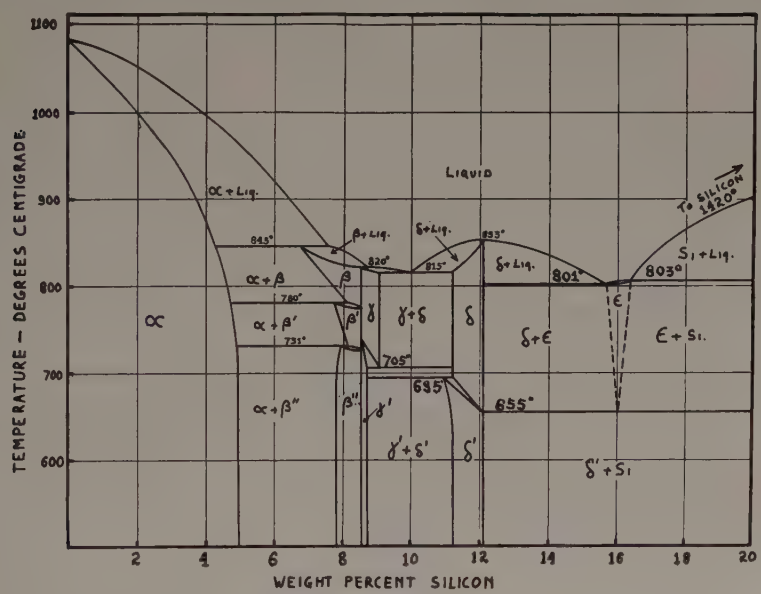

FIG. 2.—COPPER-SILICON EQUILIBRIUM DIAGRAM ACCORDING TO SANFOURCHE (1919).

Beyond the α phase, saturated at 5 per cent. silicon, there are three other distinct phases; β, between 7.9 and 8.6 per cent. silicon, supposed to undergo two polymorphic changes; γ, immediately adjoining this and also suffering a polymorphic change; and δ, which forms a eutectic with γ. This phase also undergoes a polymorphic change although the heat effect is very small. Instead of the eutectic indicated by Rudolfi, Sanfourche found a range of alloys melting at 801° to 802° C. and suggested the existence of a fifth phase, ϵ, at about 16 per cent. silicon. There is very little evidence to support this assumption.

Corson[4] peremptorily discards all previous work as incorrect and himself suggests a diagram which is very simple although it does not

[3] M. A. Sanfourche: Sur les alliages cuivre-silicium. *Rev. Met.* (1919) **16,** 246.

[4] M. G. Corson: Copper Alloy Systems with Variable Alpha Range. *Proc.* Inst. Metals Div. (1927) 435; Merit in Copper-silicon Alloys. *Iron Age* (1927) **119,** 353.

explain the very marked cooling curve arrests found by the previous workers. He gives no experimental details whatever. His diagram is reproduced in Fig. 3.

In a previous paper the author[5] determined with considerable accuracy the limits of the α solid solution, and the solidus and liquidus lines up to 7 per cent. silicon. The liquidus was determined by a series of cooling curves, and the solidus by the microscopic examination of specimens quenched after annealing at successively increasing temperatures.

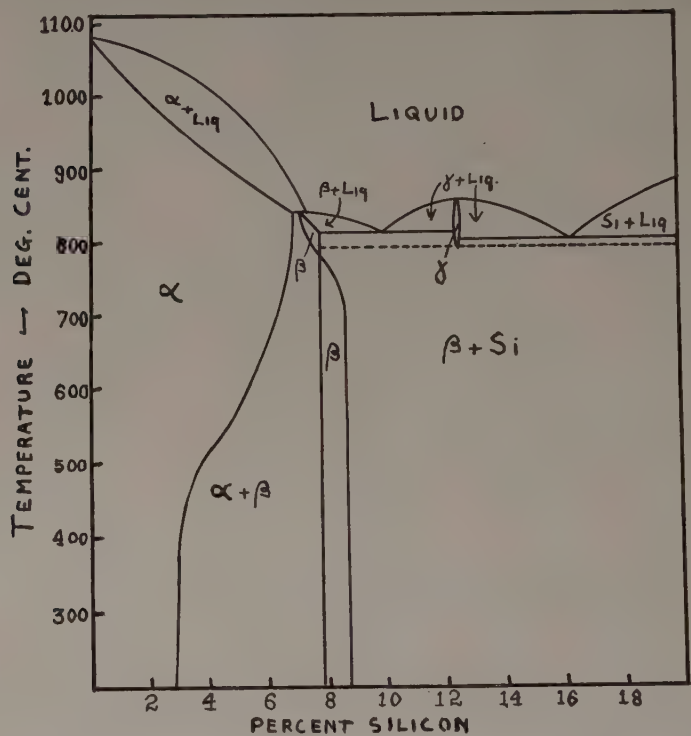

FIG. 3.—COPPER-SILICON EQUILIBRIUM DIAGRAM ACCORDING TO CORSON (1927).

The limit of the α solid solution was fixed by the microscopic examination of a very large number of samples varying in composition by steps of only 0.1 per cent., which were annealed for long periods at various temperatures and quenched. The time of annealing varied from seven or eight hours at temperatures near the melting point, to one week at 400° C. and seven weeks at 350° C. The results of these experiments are summarized in Fig. 3*a*, which is reproduced from the previous paper by kind permission of the Institute of Metals. The solubility reaches its maximum value, 6.7 per cent. silicon, between 721° and 782° C. and

[5] C. S. Smith: The α-Phase Boundary of the Copper-Silicon System. *Jnl.* Inst. Met. (1928) **40**, 359.

decreases both above and below this temperature range. At the peritectic point, α contains only 5.25 per cent. silicon, while below 782° C. the solubility decreases gradually to 3.85 per cent. at 350° C., the lowest annealing temperature used. The rapid decrease in solubility above 782° C. is of a type unusual in equilibrium diagrams, and is apparently due to the great stability of the β phase. The δ phase is evidently less

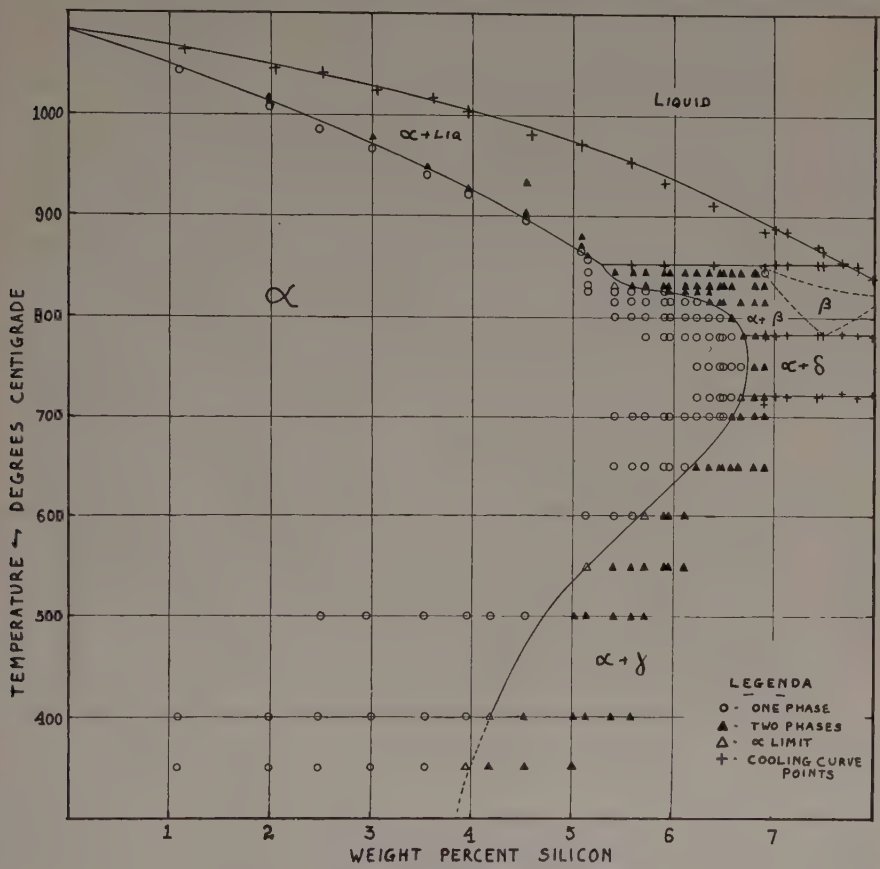

FIG. 3*a*.—α-PHASE BOUNDARY OF THE COPPER-SILICON SYSTEM ACCORDING TO SMITH (1928).

stable and permits a greater amount of silicon to go into solution. With the exception of changing the temperature of the third horizontal line from 721° C. to 726° C., the results of this work have been included in the complete diagram shown in Figs. 7 and 8 of the present paper.

When the manuscript of this paper was almost completed, a recently published diagram by K. Matuyama[6] came to the author's attention.

[6] K. Matuyama: On the Equilibrium Diagram of the Copper-silicon System. *Sci. Repts.* Tohoku Imp. Univ. [1] (1928) **17**, 665.

This diagram is reproduced in Fig. 4 and will be seen to differ in several details from the one drawn by the author. This is probably due to the wide spacing of points, for, while Matuyama had only four alloys between 8 and 10 per cent. silicon, the author made 22 alloys in this range. The liquidus differs somewhat in that the silicon eutectic occurs at 17 per cent. silicon instead of 16 per cent., as given by the author, and the almost

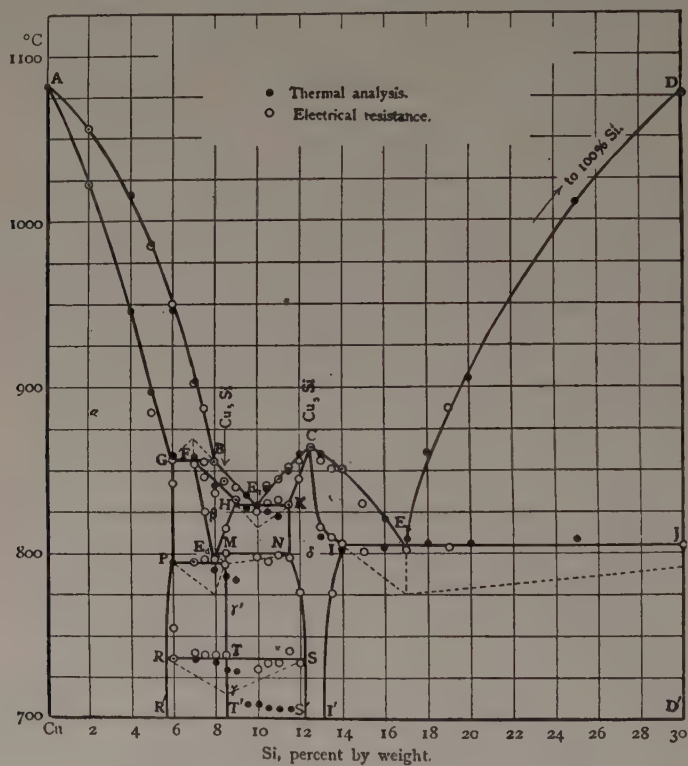

FIG. 4.—COPPER-SILICON DIAGRAM ACCORDING TO MATUYAMA (1928).

horizontal portion of the liquidus due to the author's δ solid solution is lacking. The temperatures of the various horizontals agree fairly well, but Matuyama's temperatures are generally about 5° higher. By electrical resistance methods, Matuyama found a horizontal, *MN*, at 800° C. which the author did not observe either by cooling curves or quenching experiments. As, however, quenching experiments in this range were not very complete, it is not possible definitely to state that Matuyama is in error on this point.

Experimental Work

Analysis of Materials

The alloys for the present investigation were made from electrolytic copper and the purest obtainable silicon. The latter, which was very kindly supplied by the Electro Metallurgical Sales Corpn. of New York, had the following analysis: silicon, 99.18 per cent.; iron, 0.44 per cent.; aluminum, 0.15 per cent.; calcium, 0.04 per cent.

To facilitate the melting of the alloys in small charges, large quantities of intermediate alloys with 12 per cent. and 22 per cent. silicon were first made up, and, after complete analysis, these were used in making the crucible charges. They were found to contain 0.09 and 0.12 per cent. iron respectively, no aluminum, no calcium. These latter elements had apparently been removed by oxidation during melting. The alloys with less than 12 per cent. silicon were made by melting together the necessary quantities of the 12 per cent. alloy and copper. The melts with more than this amount of silicon were made from the two alloys.

All the cooling-curve ingots and the bars from which the samples for microscopic examination were cut were analyzed for copper. On many of the alloys silicon was also determined, and after the technique had been established the two figures totaled to 100 per cent. $\pm$ 0.1 per cent. Since the copper determination is the more accurate, this element alone was determined on most of the samples, and the silicon taken by difference. In all cases duplicate determinations of copper were made, and if these did not agree sufficiently closely, further determinations were made until a satisfactory check was obtained. No correction was made for the iron present, and in reality the diagram determined is a diagonal section of the ternary copper-silicon-iron diagram very close to the copper-silicon side, with the iron varying uniformly from zero to 0.12 per cent.

Method of Analysis

For the determination of copper, duplicate 1.0-g. samples were weighed out and each dissolved in 35 c.c. of a solution containing 1700 c.c. water, 500 c.c. sulfuric acid (1.84 sp. gr.) and 300 c.c. of nitric acid (1.42 sp. gr.). The solutions were then diluted to 150 c.c. and electrolyzed for 14 hr. with a current of 0.5 amp. at 10 volts. Stationary platinum-gauze electrodes and wire anodes were used. Alloys containing 9 per cent. or more silicon were not completely soluble in the dissolving solution, and to these 2 c.c. of hydrofluoric acid was added, after which the solution was evaporated to fumes, taken up with 7 c.c. 1-1 nitric acid, diluted to 150 c.c. and electrolyzed as before. Silicon was rarely determined on these high-silicon alloys.

The silicon determination was made on 0.5-g. or 1.0-g. samples which were dissolved in 25 c.c. of the given solution. The mixture was then evaporated to dense fumes of sulfur trioxide, after which it was taken up with water, boiled and filtered on No. 42 Whatman paper. The residue was ignited in a platinum crucible, weighed, treated with hydrofluoric acid and again weighed. The loss in weight represented silica and was converted to silicon percentage in the sample.

Thermal Analysis

Cooling curves were made of a complete series of the alloys up to 20 per cent. silicon. The crucible charges used varied in composition by steps of 0.1 per cent. in the range between 7 and 10 per cent. silicon, 0.2 per cent. between 10 and 12.5 per cent., and a wider spacing up to 20 per cent. silicon. The oxidation losses on melting were rather variable, consequently an even series was not obtained, and no cooling curves were made on alloys between 9.0 and 8.5 per cent. silicon, but otherwise the alloys were fairly uniformly spaced.

The ingots for the cooling curves weighed 200 g. in the range up to 13 per cent. silicon, and 180 g. beyond this. They were melted and cooled under a covering of charcoal in tall graphite crucibles in a vertical electric tube furnace. Chromel-alumel thermocouples, 0.040 in. dia., were used, in connection with a Leeds and Northrup potentiometer reading to 0.001 mv. The cold junction was kept in a vacuum bottle filled with ice, and couples were calibrated frequently against the following melting points.

	°C.
Copper	1083.0
Silver	960.5
Copper-silver eutectic (78 per cent. silver)	778.0
Aluminum	658.9
Zinc	419.4

Successive calibrations were found to differ by less than a degree, and, including errors of calibration, plotting, and from all sources it is unlikely that the maximum error in any case is more than $\pm 5°$ C.

The thermocouples were mounted in twin-bore alundum tubing, ¼ in. dia., the junctions projecting at the end. To protect the couples from contact with the molten metal, short sheaths machined from arc-lamp carbon were used. These had walls about 1/16 in. thick and a narrow projection at the end to keep the junction about ¼ in. from the bottom of the crucible, to insure its being well surrounded by metal. The crucibles were tall and narrow and the couple was immersed to a depth of about 2 in. The arrangement is shown diagrammatically in Fig. 5. Sharp arrests with very little lag were obtained by this method.

The readings were taken for plotting by the inverse rate method, a seconds clock being read each time successive falls of temperature equivalent to 0.05 mv. had occurred. The rate of cooling before solidification commenced was between 4° and 6° C. per minute and was controlled by maintaining a small steady current through the furnace. When investigating the changes in the solid state the rate of cooling was never more than 4° C. per min., and in some special cases was as little as 2° C. per min. to reduce undercooling as much as possible.

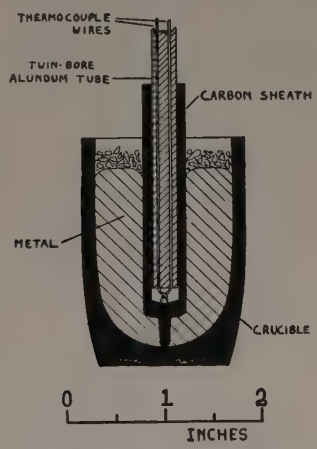

FIG. 5.—ARRANGEMENT OF CRUCIBLE AND THERMOCOUPLE FOR COOLING CURVES.

The arrests observed are assembled in Table 1 and are plotted in the diagram, Fig. 7. Fig. 6 shows some typical cooling curves.

Annealing and Quenching Experiments

Although cooling curves were used to determine the liquidus and the temperatures of the various horizontal lines in the diagram, the composition ranges over which the various phases existed were determined by the microscopic examination of a large series of quenched samples. The samples were in the form of pieces sawn or broken off chill-cast bars ½ in. dia. and 6 in. long. The alloys with more than 7.5 per cent. silicon were too brittle to be sawn and the alloys undergoing the δ-γ change (8.4 to 8.7 per cent. silicon) were so brittle that they disintegrated during cooling after casting. The high-silicon alloys (ϵ) lacked this extreme fragility, although they were also very brittle, and much difficulty was experienced in obtaining a quenched sample large enough for polishing.

Samples for annealing were packed inside a thick-walled copper tube, which was placed in a horizontal electric tube furnace, specially wound and equipped with auxiliary end coils to give uniform temperature distribution. To minimize oxidation an illuminating-gas atmosphere

TABLE 1.—*Summary of Thermal Analysis*

No.	Silicon, Per Cent.	Temperature of Arrests					
		Primary	Eutectic or Peritectic	Solid Transformation			
		° C.	° C.	1 ° C.	2 ° C.	3 ° C.	4 ° C.
12	5.09	971	851	b	b	c	c
13	5.59	952	851	c	c	c	c
14	5.92	932	851	781	c	c	c
15	6.41	911	851	b	b	c	c
24	6.82	884	852	782	716 (739)	c	c
16	7.03	887	852	782	721	c	c
23	7.15	884	852	782	726 (736)	c	c
25	7.43	873	852	782	720	c	c
26	7.45	869	851	781	720	c	c
27	7.50	865	851	782	721 (739)	c	c
29	7.69	853	b	781	726	c	c
28	7.85	850	b	780	720	c	c
18	8.00	839	b	780	725	b	c
30	7.98	849	b	780	721	b	c
31	8.09	845	b	781	724	b	c
32	8.25	844	b	779	721	b	c
96	8.33	c	c	780	721 (727)	b	b
33	8.35	845	b	778	721	b	c
34	8.35	840	b	776	723	b	c
35	8.45	839	b	781	726	710	c
36	8.48	836	b	782	724	710	c
37	8.51	831	824	779	719	710	c
41	8.95	824	b	b	714	710	c
39	9.02	825	b	b	720	709	c
40	9.06	824	b	b	715	710	c
20	9.14	823	b	b	b	707, 670	c
42	9.15	823	b	b	b	706	c
100	9.36	c	c	c	713	700 (706)	b
43	9.36	822	b	b	b	704	c
44	9.45	822	b	b	b	702	c
21	9.70	822	b	b	b	701	c
46	9.70	822	b	b	711	704, 678	c
47	9.79	821	b	b	b	701, 680 (738)	c
48	9.90	822	b	b	c	c	c
50	10.29	835	819	b	b	699, 690	c
101[a]	10.68	c	c	c	b	717 (738)	620 (623)
51	10.85	848	820	c	c	c	c
52	11.15	855	820	b	b	700, 660	c
98[a]	11.22	c	c	c	b	710	6 6 (624)
53	11.33	855	820	c	c	c	c
54	11.59	858	b	b	b	652	b
55	11.77	857	b	c	c	c	c
56	12.16	858	b	c	c	c	c
57	12.22	858	b	b	b	b	b
58	12.29	859	b	c	c	c	c
59	12.42	859	797	c	c	c	c
60	12.69	857	796	c	c	c	c
61	13.01	855	800	b	b	b	556
99[a]	13.18	c	c	c	b	b	552 (559)
62	13.48	851	801	c	c	c	c
63	14.42	842	801	b	b	b	557
64	14.94	832	801	c	c	c	c
65	15.36	824	802	c	c	c	c
66	15.77	811	802	b	b	b	556, 546 (558, 551)
67	16.24	b	802	c	c	c	c
74	16.27	808	803	c	c	c	c
68	16.85	825	803	b	b	b	558, 548
69	17.69	853	802	c	c	c	c
70	17.86	865	802	c	c	c	c
71	18.44	872	803	c	c	c	c
72	20.16	913	802	c	c	c	c

Temperatures in parentheses indicate arrests on heating curves.

[a] = Special ingot solidified quickly to prevent segregation. Annealed 1 hr. immediately below solidus before cooling.

b = Arrest absent.

c = Readings not taken at this temperature.

was used for most of the experiments, although in the earlier work on the α alloys the furnace was merely packed with charcoal and sealed. Oxidation occurred to a smaller extent in illuminating gas but even then was an important factor. When gas was used, a heavy deposit of carbon formed on the alundum furnace core and in time short-circuited the windings and had periodically to be burned out.

A bare thermocouple rested directly against the specimens inside the tube and the temperature was controlled and recorded by a Leeds and

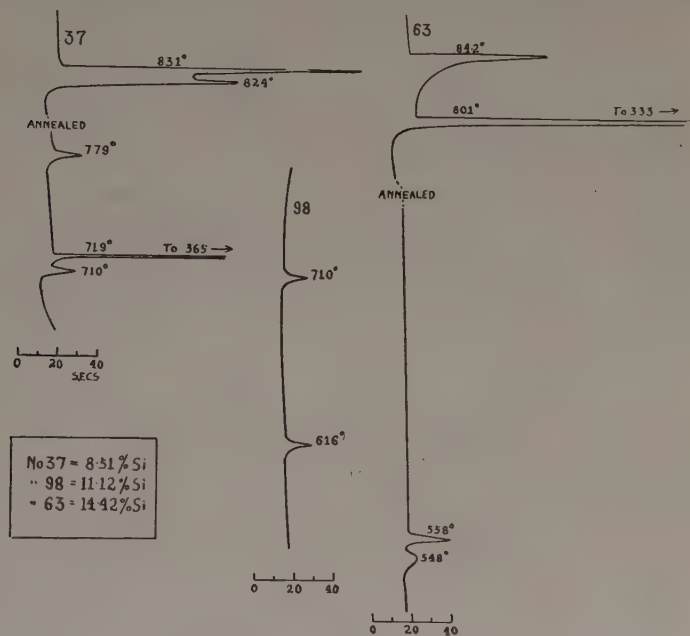

FIG. 6.—TYPICAL COOLING CURVES OF COPPER-SILICON ALLOYS.

Northrup potentiometer controller. An ice cold-junction was used, and the nickel coil in the controller intended to compensate for temperature changes was replaced by one of manganin. The temperature was kept within $\pm 3°$ C. of that desired but errors of calibration and adjustment may have resulted in a rather larger error, certainly less than $\pm 10°$ C. When the desired time of annealing had elapsed the furnace was opened, and the copper tube removed and rapidly plunged into a deep bath of water.

During the first annealing of high-silicon alloys, particularly in the δ range, considerable difficulty was experienced in obtaining a uniform structure throughout the specimens and in duplicating the results. This was finally traced to oxidation of the surface of the specimens, accompanied by rapid diffusion of silicon from the center to the outside

to make up for the loss. Oxidation proceeded very rapidly in the carbon monoxide-nitrogen atmosphere produced by the use of charcoal, and somewhat slower in illuminating gas. It was accompanied by a deposition of both carbon and silica on the surface of the specimen, and is

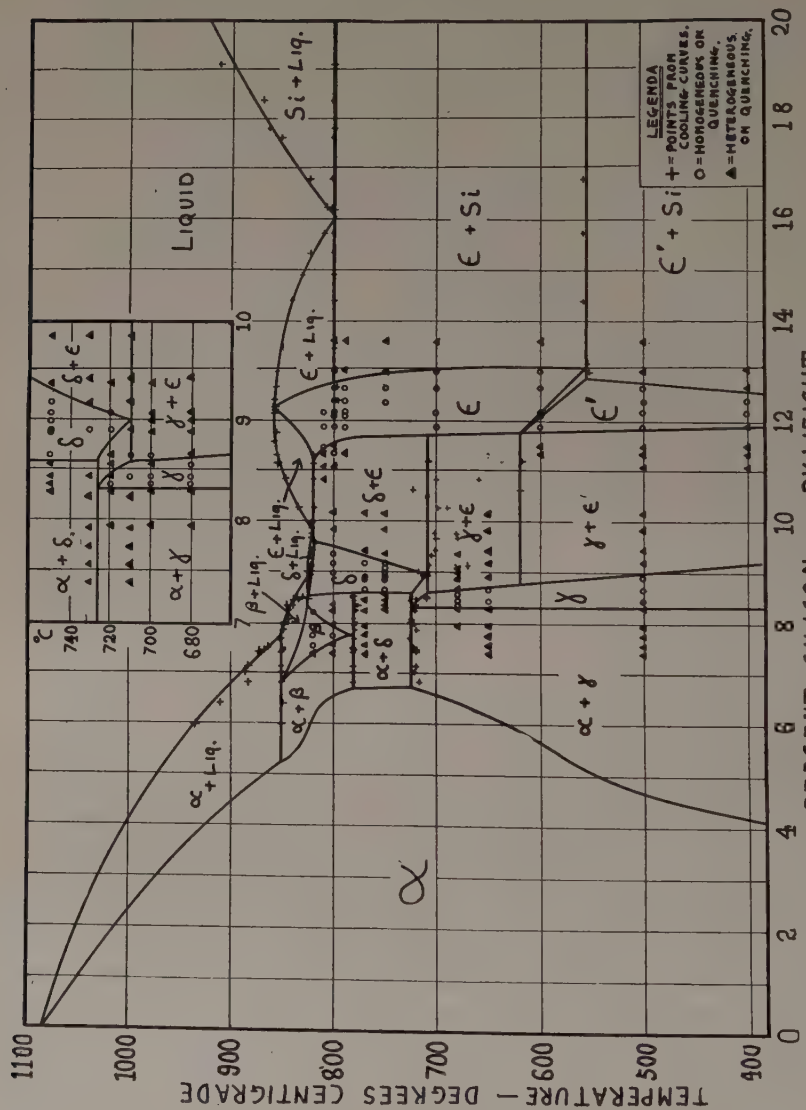

Fig. 7.—Equilibrium diagram showing experimental points.

thought to have been due to reduction of carbon monoxide by the silicon, the copper remaining unaffected. The rate of diffusion was so great that it would penetrate about ⅛ in. after 3-hr. treatment at 750° C. in illuminating gas. Owing to the lack of a vacuum furnace, the difficulty

could be overcome only by using a very short time of annealing. Between 2 and 4 hr. were given, and short though this was, it was sufficient time for the samples to attain equilibrium because of the high rate of diffusion.

The deoxidized exterior of the annealed samples could often be chipped off and separated from the interior. In one case the two parts were analyzed and found to contain 10.00 per cent. silicon in the center and 8.64 per cent. silicon on the outside. This deep oxidized zone was found principally in the alloys containing δ solid solution, and it is interesting to note that the analysis of the outer shell of the sample mentioned above corresponds exactly to the copper-rich limit of this constituent. The depth of the silicon removal in the ϵ alloys was much smaller than in the δ and $\delta + \epsilon$ alloys and did not cause so much trouble.

A summary of the microstructure observed in the annealed and quenched samples is given in Tables 2 and 3 and in the diagram, Fig. 7. It should be mentioned that β was never retained as a homogeneous phase after quenching, but it always decomposed and showed a well-defined eutectoid structure. The δ solution similarly decomposed except under the most severe quenching. In Tables 2 and 3 and Fig. 7 such decomposition has been ignored and specimens showing a purely eutectoidal structure with no traces of hypereutectoid or hypoeutectoid constituents have been described as homogeneous.

TABLE 2.—*Microstructure of Annealed and Quenched Samples (β, γ and δ Ranges)*

Number		26	28	30	32	18	34	33	35	37	38	39	41	40	42	20	44	45	46	49	50
Silicon, Per Cent.		7.40	7.57	7.75	7.94	7.96	8.25	8.30	8.38	8.45	8.58	8.67	8.89	8.92	9.00	9.09	9.19	9.38	9.42	9.85	10.29
Temp. °C.	Time, Hours																				
820	4	x	o	o			o														
800	4	x	x	o	x		x			x				o			o	o		x	x
770	4	x	x	x	x		x			x		o		o			o		x		x
750	2							x	x	x	x	o	o	o	o	o	o	x		x	x
730	7	x	x	x	x		x			x				o			x		x	x	x
720	2					x		x	o	x	x	x	x	o		o		x			
710	4	x	x	x	x		x			o		o		x			x		x	x	x
700	2					x		x	o	o	x	o	x		x	x		x			
680[a]	2					x		x	o	o	o	x	x		x	x		x			
650[a]	3	x	x	x	x			x		o		o		x			x			x	x
500[a]	13	x	x	x	x			x		o		o		o			x		x	x	x

o = One phase.
x = Two phases.

[a] Cast samples annealed directly at temperatures noted, except samples marked [a] which were first annealed 2 to 4 hr. at 750° C. and slowly cooled to temperatures noted.

A sample consisting entirely of eutectoid with no proeutectoid constituent is described as homogeneous. All β samples and many δ samples had decomposed during quenching.

TABLE 3.—*Microstructure of Annealed and Quenched Samples* (ϵ *Range*)

Number		52	53	55	54	56	57	58	59	60	61	62	63
Silicon, Per Cent.		10.86	11.11	11.36	11.49	11.90	12.12	12.19	12.49	12.69	13.01	13.60	14.42
Temp., ° C.	Time, Hours												
400[a]	11		x	x	x	x		o	o	x	x	x	x
500[a]	13		x	x	x	o		o	o	o	x	x	
600[a]	2			x	x	o	o	o	o	o	o	x	x
700	3			x	x	o		o	o	o	o	x	
750	4								o	o	x	x	
790	4			x		o	o	o	o	o	x	x	x
800	3		x	o	x	o	o	o	o	o	x	x	
807	2	x	x	x	o	o		o					

o = One phase.
x = Two phases.

[a] Cast samples annealed directly at temperatures noted, except samples marked [a] which were first annealed 2 to 4 hr. at 750° C. and slowly cooled to temperatures noted.

THE DIAGRAM

All the points determined by thermal and microscopic means are assembled in Fig. 7. To avoid confusion of the points, the results of the microscopic examination of alloys near the junction of the γ and δ fields are plotted by themselves on a larger scale at the top of the figure, and the diagram is redrawn without the experimental points in Fig. 8. The various phases will be considered individually in detail.

The Alpha Phase

The limits of the α phase were described in the author's previous paper[7] and need no further comment here.

The Beta Phase

This constituent is formed at 852° C. by the reaction of α with 5.25 per cent. and liquid with 7.7 per cent. silicon. Its composition at the triple point is 6.8 per cent. silicon, exactly as found by Sanfourche. This point is determined as being the composition at which the 852° C. arrest on the thermal curves reaches its maximum intensity, and beyond which solidification proceeds below this temperature.

This composition is further confirmed by the structure of samples with 6.81 and 6.91 per cent. silicon quenched from 845° C., the latter showing no proeutectoid α (see Fig. 9) and the former only a trace. At 824° C., when in equilibrium with γ, β is saturated at 8.4 per cent. silicon, but the solubility for both copper and silicon decreases rapidly, until at

[7] *Loc. cit.*

782° C. β with 7.75 per cent. silicon decomposes eutectoidally into $\alpha + \delta$. This composition is confirmed by both microscopic and thermal means.

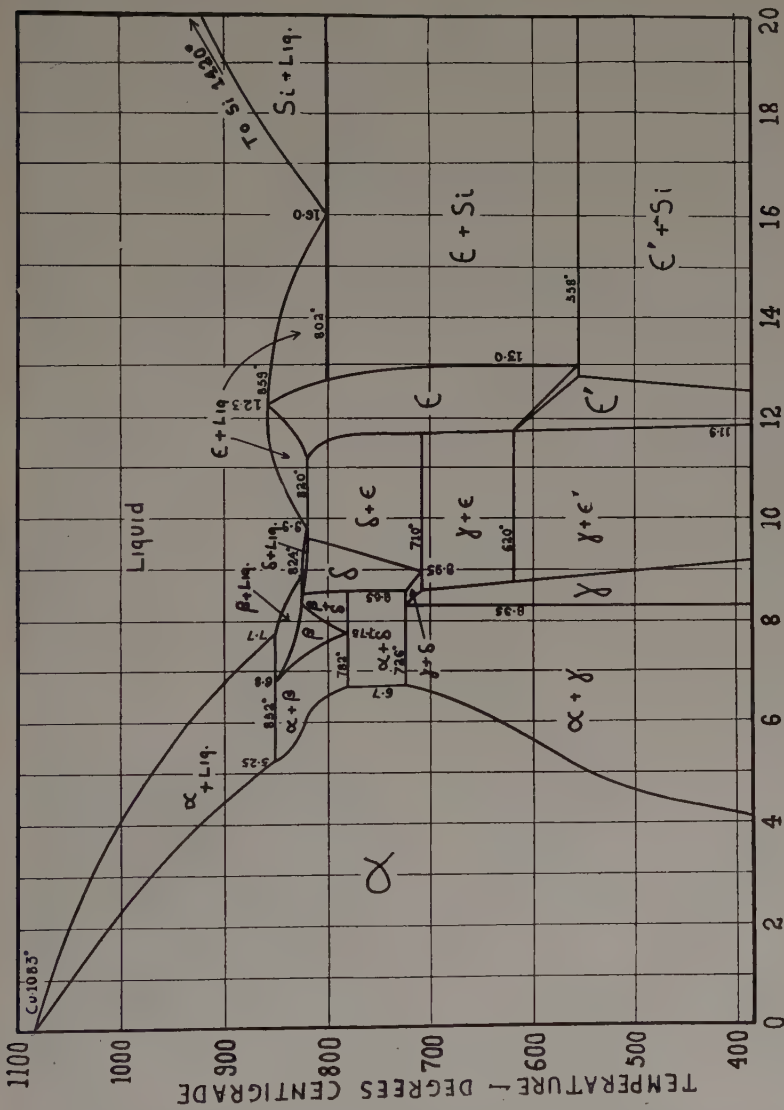

FIG. 8.—EQUILIBRIUM DIAGRAM OF THE COPPER-SILICON ALLOYS.

No attempts were made to determine by quenching experiments the solidus of the β phase, but the termination of the arrests on the cooling curves show it to be of the form drawn in the diagram.

As mentioned earlier, the β phase can not be retained as a homogeneous constituent even after the most rapid quenching, but it always

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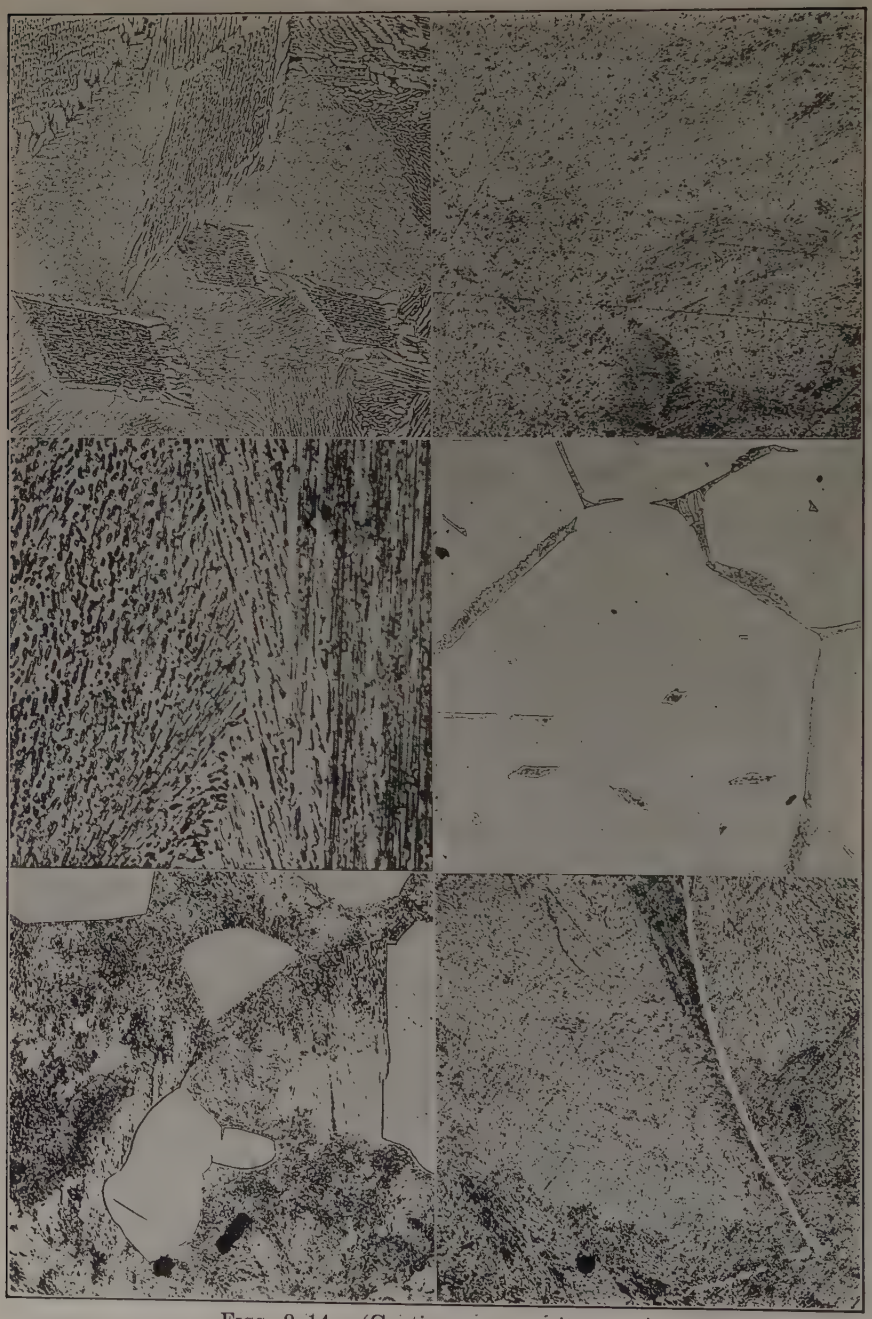
11 12

13 14



FIGS. 9–14.—(Captions on opposite page.)

decomposes eutectoidally into $\alpha + \delta$. The eutectoid is very finely divided in alloys of about the eutectoid composition, but in the case of alloys which only become homogeneous at high temperatures, the excess of α or δ precipitated during cooling along the sloping β phase boundary results in a rather coarse structure. Figs. 9* and 10 show this well, the former being of saturated β (6.91 per cent. silicon) quenched from 845° C. and the latter of β of eutectoid composition (7.75 per cent. silicon) quenched from 800° C. The fine eutectoid is shown again at a higher magnification in Fig. 11. The appearance of the β eutectoid when in equilibrium with α is shown in Figs. 12* and 13 and with δ in Figs. 14 and 15.

The best etching reagent found for the eutectoid was a saturated solution of potassium bichromate in 10 per cent. sulfuric acid with the addition of 2 per cent. of saturated sodium chloride solution.

The Delta Phase

At 824° C., saturated β (approximately 8.4 per cent. silicon) reacts with liquid and produces δ with 8.60 per cent. silicon. This phase exists alone up to 9.7 per cent. silicon, beyond which point the eutectic of δ and ϵ appears, melting at 820° C. The boundary of the δ phase on the copper-rich side remains almost vertical until it encounters the $\gamma + \delta$ field at 726° C., after which it rapidly changes with fall of temperature until at 710° C., where it decomposes to $\gamma + \epsilon$, δ contains 8.95 per cent. silicon. The solubility on the silicon-rich side varies uniformly from the eutectoid point to δ saturated with 9.7 per cent. silicon at 820° C. The very sharp arrests on the cooling curves show that the solidus and liquidus of the δ phase are less than 2° C. apart at any point.

The quenching experiments determined with a fair degree of accuracy the limits of composition of the δ phase, but some difficulty was experienced in determining the exact temperature of the $\delta \rightarrow \gamma + \epsilon$ eutectoid. While in the $\gamma + \delta$ range the change occurred definitely at 710° C. with no undercooling, the arrests when ϵ was present were very erratic and often appeared double after considerable undercooling. Repeat curves on the same ingot frequently showed totally different results. Such behavior is not quite concordant with the rapid rate of decomposition, which often prevented the retaining of microscopically homogeneous δ after quenching, and it was at first thought that there was another phase in the $\delta + \epsilon$ area. No sign of this was observed on the microsamples,

* Figs. 9 and 12 reproduced by kind permission of the Institute of Metals.

FIG. 9.*—No. 93 (6.91 PER CENT. SI). QUENCHED 845° C. β EUTECTOID. × 100.
FIG. 10. —No. 30 (7.75 PER CENT. SI). QUENCHED 800° C. β EUTECTOID. × 100.
FIG. 11. —No. 32 (7.94 PER CENT. SI). QUENCHED 820° C. β EUTECTOID. × 500.
FIG. 12.*—No. 85 (6.11 PER CENT. SI). QUENCHED 825° C. $\alpha + \beta$ EUTECTOID. × 100.
FIG. 13. —No. 26 (7.40 PER CENT. SI). QUENCHED 800° C. $\alpha + \beta$ EUTECTOID. × 100.
FIG. 14. —No. 32 (7.94 PER CENT. SI). QUENCHED 800° C. $\delta + \beta$ EUTECTOID. × 100.
All specimens etched with potassium bichromate and sulfuric acid.

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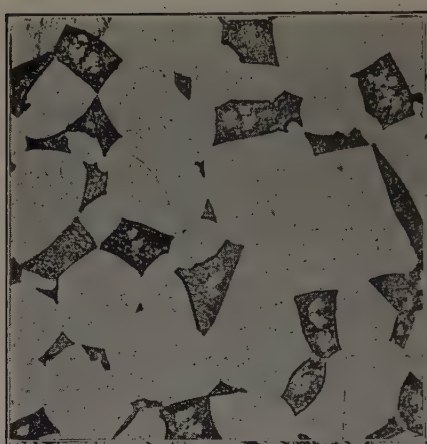

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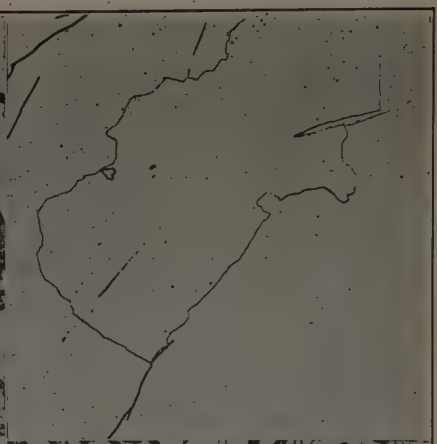

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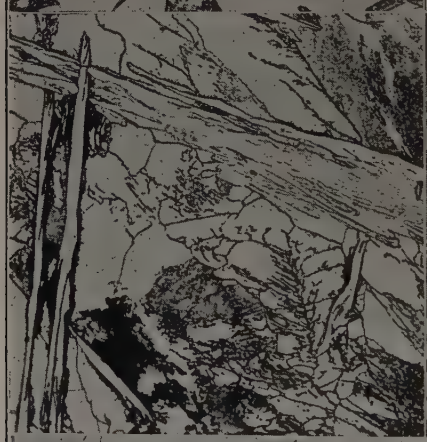

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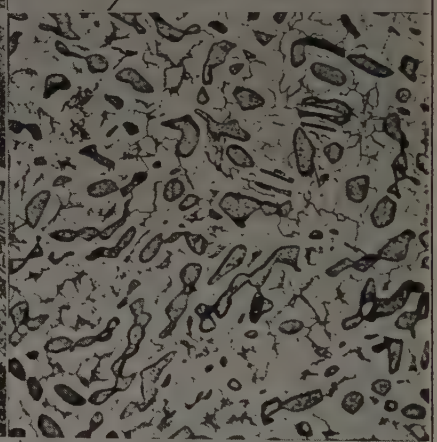

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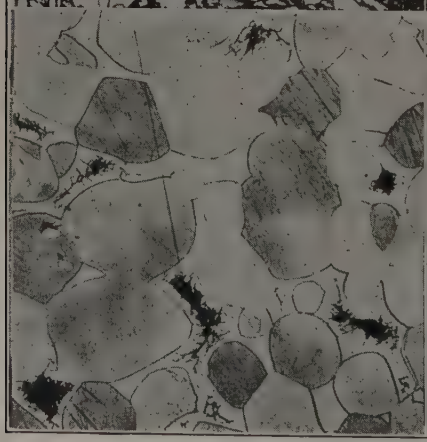

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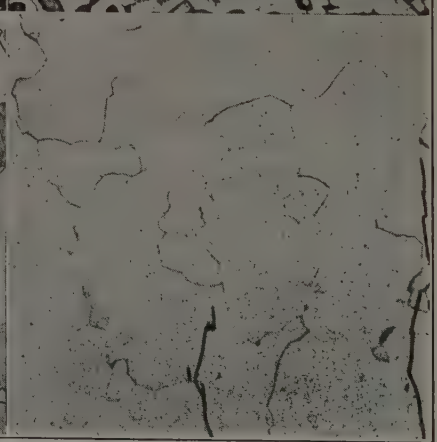


FIGS. 15–20.—(Captions on opposite page.)

which were entirely in accord with the diagram as shown. The temperature of 710° C. was finally adopted as that of the eutectoid, as it was at this temperature that the most well-defined arrests appeared. It will be noted in Table 2 that the microsamples quenched from 710° C. showed the structures to be expected in samples quenched immediately below this temperature. This is thought to have been due to a slight inaccuracy of the pyrometer controlling the anneal.

The δ phase, similar to β, could not always be retained as a homogeneous phase at room temperature. Small rapidly quenched samples often appeared partly homogeneous, particularly on quenching from a point well within the δ area, but decomposition usually occurred under normal conditions. The decomposed samples were sometimes acicular and sometimes finely granular in appearance. Both forms of decomposition, somewhat reminiscent of martensite and sorbite in steels, are shown in Fig. 17, while Fig. 16 shows an undecomposed area in a sample quenched from a higher temperature. The acicular eutectoid structure always appeared in samples containing γ, but the sorbitic type was more common in alloys consisting of pure δ, particularly those of about eutectoid composition. Fig. 18 shows partly decomposed δ in conjunction with α and Fig. 19 is of an alloy with 9.85 per cent. silicon quenched from 770° C., consisting of δ, which shows slight decomposition, and ϵ.

The best etching reagent for the δ alloys was found to be a 20 per cent. solution of ferric chloride in 1-4 hydrochloric acid. This reagent worked extremely well and a deep etch could be given in order to remove polishing scratches without destroying the sharpness of the structure.

The Gamma Phase

The γ phase is formed at 726° C. by a "peritectoid" reaction between δ and α. On cooling curves the reaction often showed undercooling but by very slow cooling the temperatures became more constant and reproducible. The temperature was given in the author's paper[8] on the α phase boundary as 721° C., but further work on the alloys near the pure γ field have shown that 726° C. is more nearly the correct temperature.

[8] *Loc. cit.*

FIG. 15.—No. 37 (8.45 PER CENT. Si). QUENCHED 800° C. $\delta + \beta$ EUTECTOID. ETCHED $K_2Cr_2O_7 + H_2SO_4$. × 100.

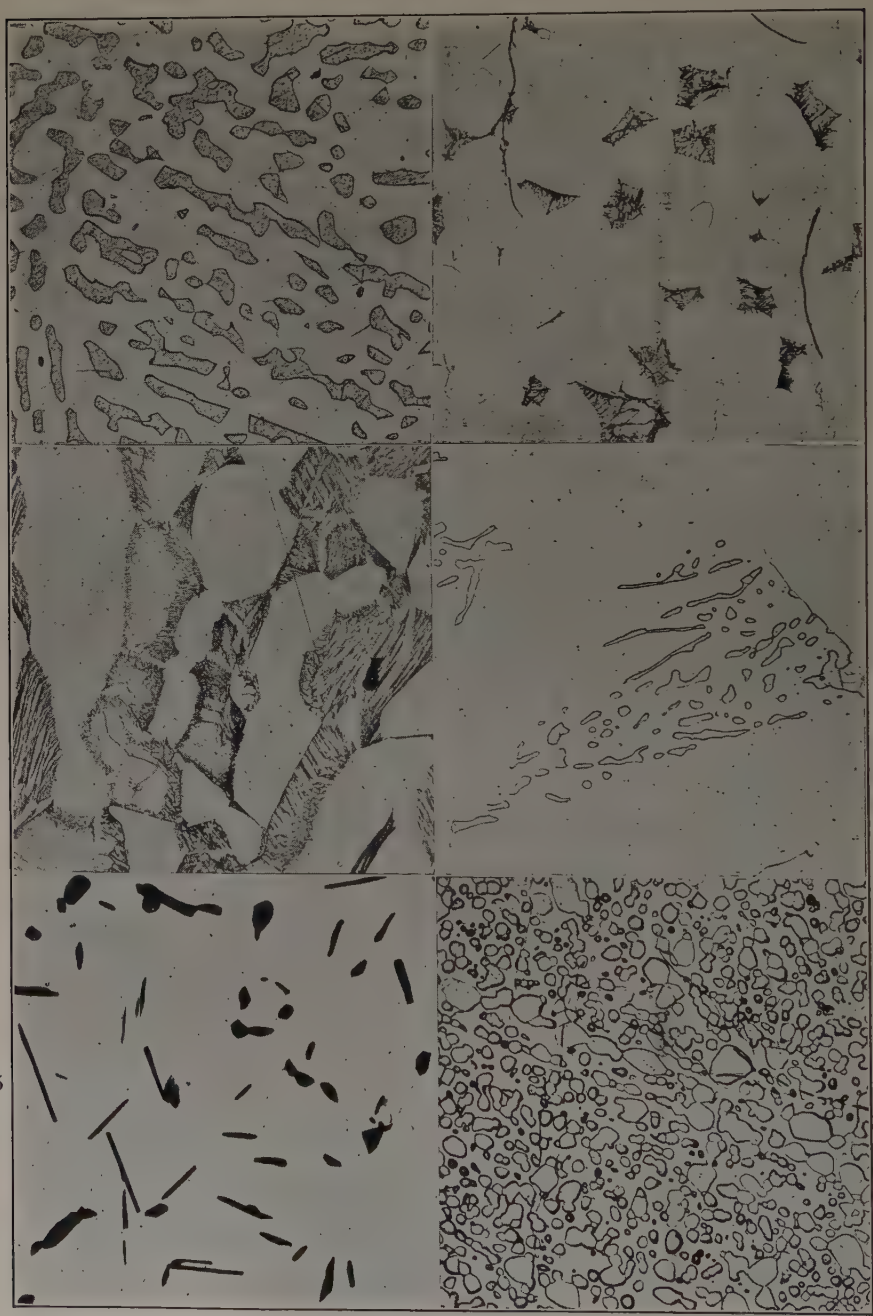
FIG. 16.—No. 20 (9.09 PER CENT. Si). QUENCHED 750° C. HOMOGENEOUS δ. ETCHED $K_2Cr_2O_7 + H_2SO_4$. × 100.

FIG. 17.—No. 41 (8.89 PER CENT. Si). QUENCHED 750° C. DECOMPOSING δ. ETCHED $FeCl_3$. × 100.

FIG. 18.—No. 35 (8.38 PER CENT. Si). QUENCHED 750° C. α + DECOMPOSING δ. ETCHED $FeCl_3$. × 100.

FIG. 19.—No. 49 (9.85 PER CENT. Si). QUENCHED 770° C. ϵ + DECOMPOSING δ. ETCHED $FeCl_3$. × 100.

FIG. 20.—No. 35 (8.38 PER CENT. Si). QUENCHED 700° C. HOMOGENEOUS γ. ETCHED $K_2Cr_2O_7 + H_2SO_4$. × 100.



FIGS. 21–26.—(Captions on opposite page.)

At the triple point γ contains 8.35 per cent. silicon, which is the composition of the copper-saturated phase at all temperatures. On the silicon-rich side, γ rapidly dissolves silicon between 726° and 710° C. and more slowly after this as the temperature falls. These points were fixed with little doubt by the quenching experiments.

Under the microscope, γ is in appearance very similar to δ, although, of course, it never shows eutectoidal decomposition. It can be etched by either ferric chloride or potassium bichromate with about equally good results. In the pure state it is shown in Fig. 20, which is of any alloy with 8.38 per cent. silicon annealed at 700° C. This should be compared with Fig. 18, which is of the same alloy after quenching from the $\alpha + \delta$ range (750° C.). Fig. 21 shows γ in equilibrium with α at 720° C., and Figs. 22 and 23 show γ with the δ eutectoid at the same temperature. Figs. 24 and 25 show precipitation of ϵ at 680° and 700° C. in an alloy with 8.89 per cent. silicon, which becomes homogeneous γ at lower temperatures and homogeneous δ at higher temperatures. Fig. 24 shows the sample after slowly cooling from 750° C. to 680° C. and quenching after 2 hr. at this temperature. It shows the remains of the $\delta \rightarrow \gamma + \epsilon$ eutectoid coarsely spheroidized. Fig. 25 is the same alloy, previously homogeneous γ, reheated at 700° C. for 1 hr. The eutectoid point was not passed, and the ϵ has been thrown out of solution along the crystallographic planes. Fig. 26 is of an alloy containing 9.38 per cent. silicon quenched from the middle of the $\gamma + \epsilon$ range and shows the characteristic rounded form of ϵ, while Fig. 27 is an alloy with 11.49 per cent. silicon annealed at 400° C. and shows γ in conjunction with ϵ'.

The Epsilon Phase

Cooling curves show that δ forms a eutectic with the next phase ϵ, at 820° C. and 9.9 per cent. silicon. The melting point of the eutectic differs but slightly from that of δ, but beyond the eutectic point the liquidus rises to a flat maximum at 859° C. and 12.3 per cent. silicon, corresponding to the melting of the ϵ phase, which also forms a eutectic with silicon. Small arrests due to the ϵ-silicon eutectic were observed on cooling curves of alloys with 12.49 per cent. and 12.69 per cent. silicon, but annealing experiments showed that the solubility at the eutectic temperature was more than this and became even greater at slightly

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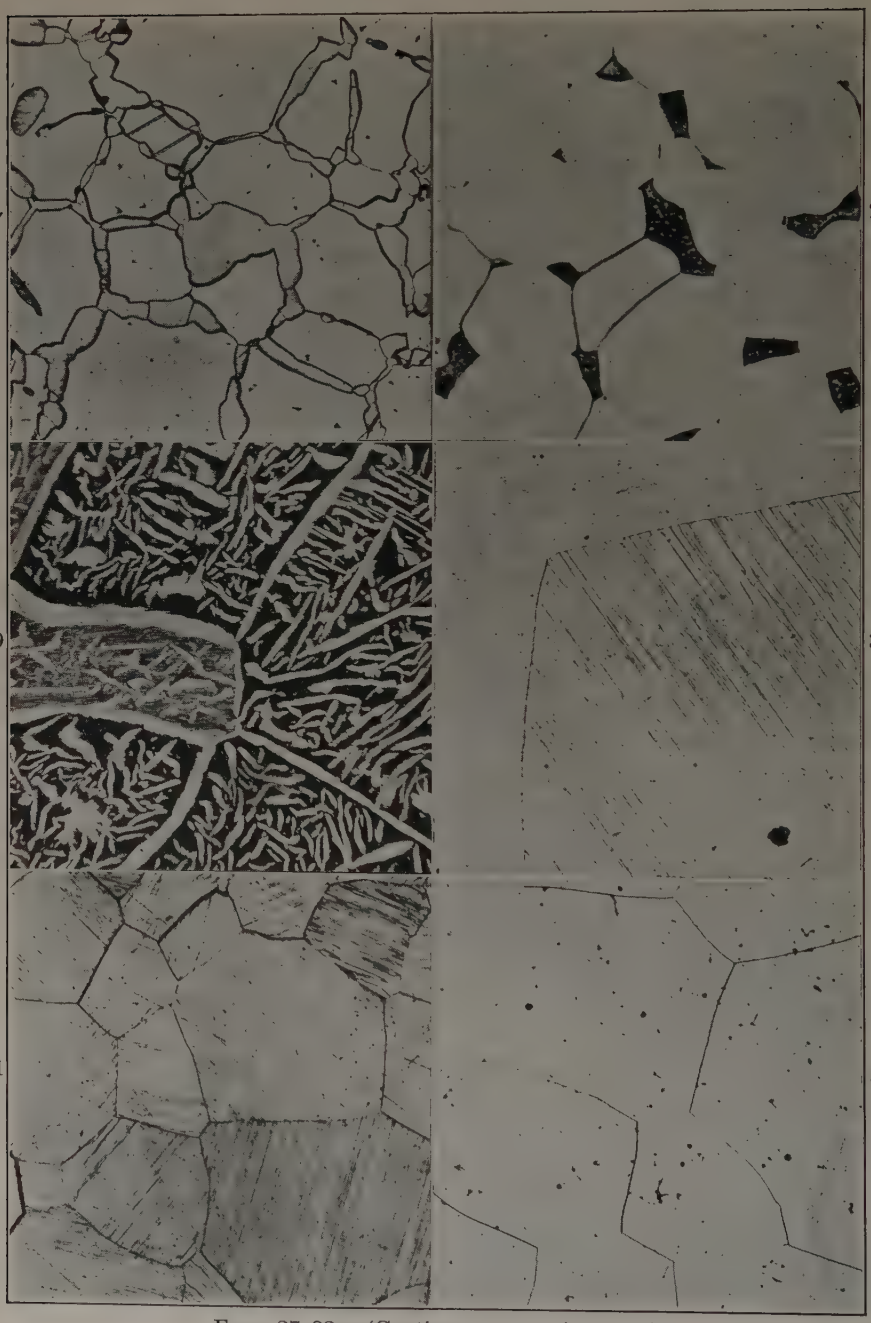
FIG. 21.—No. 33 (8.30 PER CENT. Si). QUENCHED 720° C. $\alpha + \gamma$. × 100.
FIG. 22.—No. 37 (8.45 PER CENT. Si). QUENCHED 720° C. γ + DECOMPOSED δ. × 100.
FIG. 23.—No. 39 (8.67 PER CENT. Si). QUENCHED 720° C. γ + DECOMPOSED δ. × 100.
FIG. 24.—No. 41 (8.89 PER CENT. Si). SLOWLY COOLED 750° C. TO 680° C. QUENCHED 680° C. $\gamma + \epsilon$. × 100.
FIG. 25.—No. 41 (8.89 PER CENT. Si). QUENCHED 700° C. $\gamma + \epsilon$. × 100.
FIG. 26.—No. 45 (9.38 PER CENT. Si). QUENCHED 680° C. $\gamma + \epsilon$. × 100.

All specimens etched with ferric chloride.



FIGS. 27–32.—(Captions on opposite page.)

lower temperatures. The solubility on the copper-rich side is also greater than that shown by the cooling curves but it rapidly decreases as the temperature falls. This can be seen by comparing Figs. 28 and 29. The former is of an alloy with 11.11 per cent. silicon quenched from 807° C. and shows ϵ with a little δ, and the latter figure is of an alloy with more silicon (11.90 per cent.) quenched from 790° C., and shows a much larger quantity of δ, precipitated throughout the grains.

Sanfourche's observation of a polymorphic change in ϵ is confirmed, although the temperatures seem to be lower than this observer found. On the copper-rich side the change occurs at 620° C., and on the silicon-rich side, 558° C. The heat effect accompanying the change is very small but the arrests were nevertheless quite well defined and showed only slight undercooling. On the silicon side, the arrests were often double, both on heating and cooling, but the effect became less on annealing and recooling the ingots, and was probably due to segregation.

Annealing experiments were not carried out at very close intervals of temperature below 750° C., but it seems a fairly safe assumption that the change in solubility from 13.0 to 12.8 per cent. silicon found between 600° C. and 500° C. should take place at the temperature of the polymorphic change as shown in the diagram, rather than progressively throughout this range. There is no similar change in composition on the copper-rich side of ϵ, where the phase boundary slopes slightly but uniformly to the left up to 750° C., after which it commences to slope more sharply until at the eutectic temperature ϵ contains 11.2 per cent. silicon.

The ϵ alloys when freshly polished were white in color but they rapidly tarnished on exposure to the air of the laboratory, particularly if they had not been etched to remove the surface film due to polishing. The bichromate etch was not very satisfactory on the samples in this range, but the acid ferric chloride solution mentioned gave excellent results. When a deep etch was used, faint striae were developed in the ϵ grains, giving clear distinction between differently oriented crystals. These markings were absent from ϵ' samples, however deeply etched. Atmospheric tarnishing was found to be very convenient for distinguishing ϵ in the presence of δ or γ, but it was generally not suitable for photography on account of its irregularity of action. Fig. 29 is of a sample etched in

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FIG. 27.—No. 54 (11.49 PER CENT. Si). QUENCHED 400° C. $\gamma + \epsilon'$. ETCHED $FeCl_3$. × 100.

FIG. 28.—No. 53 (11.11 PER CENT. Si). Quenched 807° C. $\epsilon + \delta$. ETCHED $FeCl_3$. × 100.

FIG. 29.—No. 55 (11.36 PER CENT. Si). QUENCHED 790° C. $\epsilon + \delta$. ATMOSPHERIC ETCH. × 50.

FIG. 30.—No. 56 (11.90 PER CENT. Si). QUENCHED 807° C. HOMOGENEOUS ϵ. ETCHED $FeCl_3$. × 100.

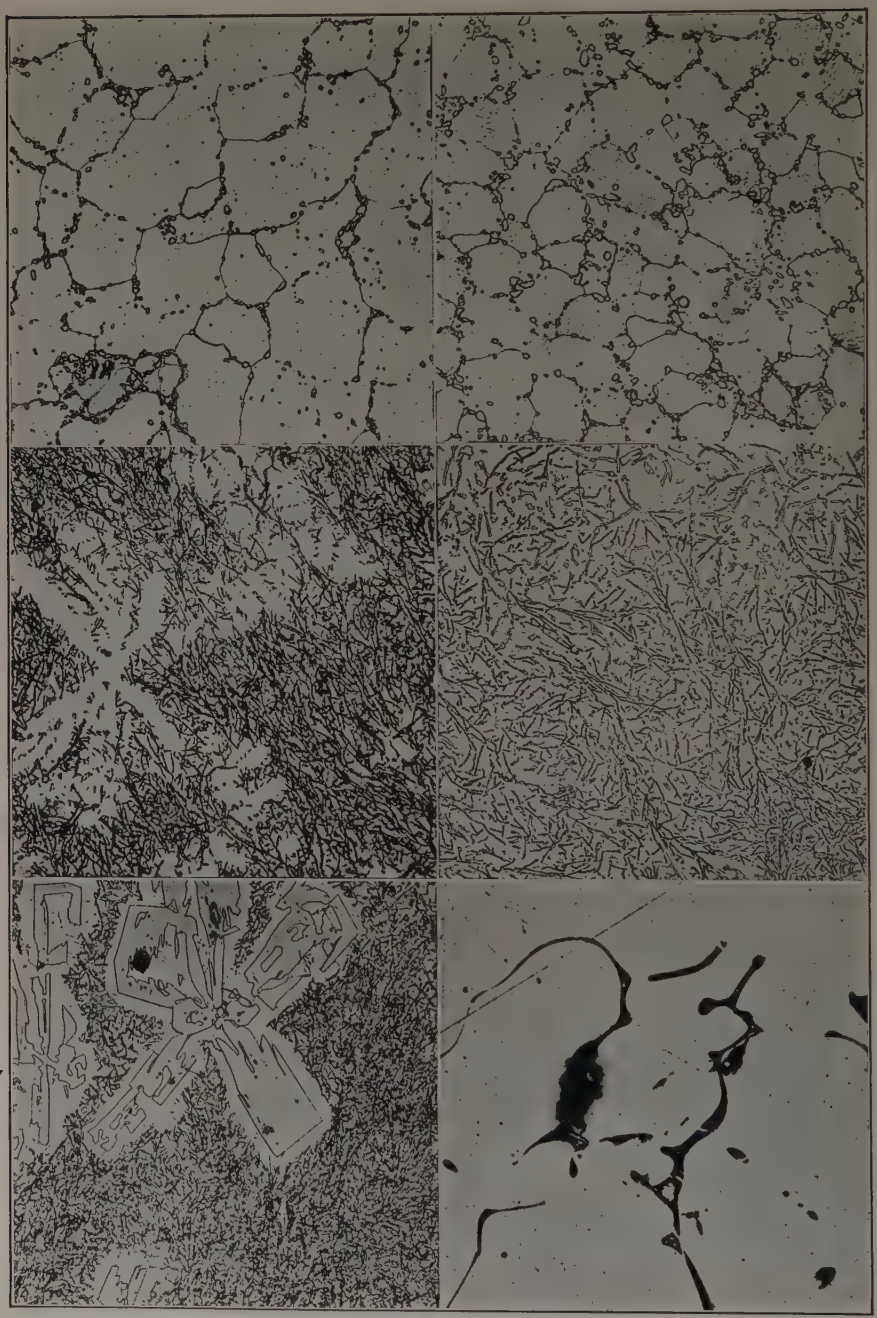
FIG. 31.—No. 61 (13.01 PER CENT. Si). QUENCHED 700° C. HOMOGENEOUS ϵ. ETCHED $FeCl_3$. × 100.

FIG. 32.—No. 58 (12.19 PER CENT. Si). QUENCHED 400° C. HOMOGENEOUS ϵ'. ETCHED $FeCl_3$. × 100.

33 34

35 36

37 38



FIGS. 33–38.—(Captions on opposite page.)

air in this manner. The dark areas are ϵ and the light are δ. The staining effect was apparently dependent on the orientation of the crystals, especially with the copper-saturated ϵ alloys, in which some grains would become dark after a few minutes and others would remain perfectly white after exposure to the atmosphere for several days. The alloys with excess silicon darkened more uniformly.

The structure of homogeneous ϵ is shown in Figs. 30 and 31. The samples were etched with ferric chloride, and the faint striae will be noticed. The striae are absent from Fig. 32, which is of ϵ' etched in the same way. ϵ or ϵ' is to be seen in equilibrium with δ or γ in Figs. 24 to 29, and in Figs. 33 to 38 with silicon. Fig. 33, showing $\epsilon' +$ silicon, should be compared with Fig. 31, which is of the same alloy after quenching from a higher temperature at which it was homogeneous ϵ.

Corson stated that the ϵ phase (which he erroneously supposed to be Cu_3Si) is unstable at temperatures much below that at which it solidifies, and supposed it to decompose rapidly into silicon and Cu_5Si (corresponding to the author's γ). In no case has any structure similar to that found by Corson been obtained, and there is no evidence whatever to indicate that ϵ decomposes other than to form ϵ' with a slight precipitation of silicon. This precipitation is readily preventable by quenching and is quite different from that observed by Corson.

Epsilon-silicon Eutectic

Rudolfi found a eutectic at 800° C. and 17.4 per cent. silicon between Cu_3Si (ϵ) and silicon, but Sanfourche found a series of alloys between 15.7 and 16.4 per cent. silicon all melting between 801° and 802° C., and suggested the formation of a solid solution decomposing at lower temperatures to δ (ϵ) and silicon. In the present work the liquidus branches drawn through the points determined by cooling curves intersect the eutectic horizontal exactly at a point. Furthermore, there is no observable difference between the temperature of the eutectic on each side of this point, and it can only be assumed that Sanfourche was in error.

FIG. 33.—No. 61 (13.01 PER CENT. SI). QUENCHED 400° C. $\epsilon' +$ SI. $\times$ 100.
FIG. 34.—No. 63 (14.42 PER CENT. SI). QUENCHED 650° C. $\epsilon +$ SI. $\times$ 100.
FIG. 35.—No. 66 (15.77 PER CENT. SI). CHILL CAST. $\epsilon + \epsilon$-SI EUTECTIC. $\times$ 100.
FIG. 36.—No. 68 (16.85 PER CENT. SI). CHILL CAST. ϵ-SI EUTECTIC. $\times$ 100.
FIG. 37.—No. 71 (18.44 PER CENT. SI). CHILL CAST. SI $+ \epsilon$-SI EUTECTIC. $\times$ 100.
FIG. 38.—No. 102 (95.61 PER CENT. SI, 4.39 PER CENT. CU). SLOWLY COOLED. SI $+ \epsilon$-SI EUTECTIC. $\times$ 100.

All specimens etched with ferric chloride.

The microstructure of cast and annealed alloys in this range also confirms the existence of the eutectic. Furthermore, alloys with more than 13 per cent. silicon after annealing at suitable temperatures consist of easily recognizable silicon in conjunction with ϵ (see Fig. 34). The structure of the chill-cast eutectic alloy is shown clearly in Fig. 36, while Fig. 35 shows primary ϵ and eutectic, and Fig. 37 shows primary silicon and eutectic.

Sanfourche mentioned that his alloys with more than 12 per cent. silicon disintegrated on standing at room temperature for a few months. This action was greatest with eutectic alloys, which crumbled to dust, and Sanfourche supposed it to be due to a slow transformation. The present author has had alloys of every composition lying around the laboratory for a period of over 6 months and in no case has any more than a heavy surface discoloration been observed.[9] It seems probable that Sanfourche's alloys contained impurities which accelerated intergranular corrosion.

Silicon

No cooling curves or annealing experiments were made on alloys with more than 20 per cent. silicon. In all alloys with more than 16 per cent. silicon, free silicon was visible, easily recognizable by its crystal form and its characteristic blue color (Fig. 37) and it is certain that the liquidus slopes smoothly from the eutectic point to pure silicon melting at 1420° C.

To determine whether there is a large solubility of copper in silicon, a single alloy of silicon with 4.39 per cent. copper was melted and allowed to cool slowly in a crucible from the liquid state. On examination under the microscope, this alloy was found to be quite free from coring and to contain appreciable quantities of eutectic. The solubility of copper in silicon is therefore less than this amount, although some of the ϵ might have been dissolved had the sample been annealed. Fig. 38 shows the structure of the sample.

Comparison with Previous Work—Nomenclature

The general form of the present diagram is similar to that drawn by Sanfourche, although it is simpler in that the β', γ' and ϵ phases of this investigator are omitted. β is shown to form a eutectoid and the limits of the α, γ and δ phases are extended considerably.

Except for the sloping α phase boundary up to 782° C. the new diagram bears very little resemblance to the diagram proposed by Corson.

[9] Note added April, 1929.—After a further 12 months' exposure to the atmosphere, an alloy with 17 per cent. silicon has partly crumbled and one with 23 per cent. has fallen completely to powder. All the alloys with less than 16 per cent. silicon, *i. e.*, those containing no primary silicon, seem to be quite stable. although heavily tarnished.

Previous investigators have all attempted to assign formulas of chemical compounds to the various phases. Rudolfi suggested Cu_3Si and $Cu_{19}Si_4$, Sanfourche $Cu_{13}Si_4$, and Corson the simple Cu_3Si and Cu_5Si. With the exception of the γ phase, which corresponds approximately to Cu_5Si, the composition of the phases determined by the present work does not fit in with any of these compounds, or with any other simple formula. The various phases have therefore been considered as solid solutions, and entirely renamed with the Greek alphabet in the order of their first appearance in the pure state.

The change at 620° to 558° C. in the ϵ phase has been considered a polymorphic one, as the change in composition is small, and the lower temperature phase called ϵ'. The change of δ to γ at 726° to 710° C. is also rather suggestive of a polymorphic transformation, but the two phases have been called δ and γ, rather than γ and γ', partly to avoid the confusion which is apt to exist between such names, and partly because the difference in composition is perhaps more than could be associated with a change of purely polymorphic nature.

Summary

The diagram, Fig. 8, in which the most important temperatures and compositions have been marked, is itself a complete summary of all the work described herein, but for convenience the various horizontal lines are listed in Table 4, with the composition of the various phases.

Table 4.—*Composition of Various Phases of Fig.* 8

Temperature ° C.	Reacting Phases
852	α (5.25%) + liquid (7.7%) → β (6.8%)
824	β (8.4%) + liquid (8.9%) → δ (8.6%)
820	liquid (9.9%) → δ (9.7%) + ϵ (11.2%)
802	liquid (16.0%) → ϵ (12.8%) + Si
782	β (7.75%) → α (6.7%) + δ (8.60%)
726	α (6.7%) + δ (8.65%) → γ (8.35%)
710	δ (8.95%) → γ (8.60%) + ϵ (11.7%)
620	ϵ (11.75%) → ϵ' (11.75%)
558	ϵ (13.0%) → ϵ' (12.8%) + Si

Acknowledgments

The author would like to express his thanks to W. H. Bassett for his kindly interest and encouragement during the prosecution of the research. He is also very much indebted to Charles H. Davis, who had general supervision over the analytical work and was of great assistance in many other ways; and to all those in the laboratory who assisted the work in any way.

DISCUSSION

C. H. Eldridge, Detroit, Mich. (written discussion).—Some years ago, from 1918–21, the Chile Exploration Co. of New York City originated a comprehensive research to find an insoluble anode to be used at Chuquicamata, Chile. This investigation was conducted by C. G. Fink, director of the company's New York laboratories. I worked upon this problem under Dr. Fink, and we covered very thoroughly all the binary silicon alloys. Copper-silicon was the first to be investigated, and although the simple alloy was unsuitable, a complex copper-silicon alloy (18 per cent. Si) with tin and lead, proved successful and is now used on a large scale at Chuquicamata. A paper by C. W. Eichrodt describes in detail the success of this anode.[10]

Fig. 39 shows corrosion loss and voltage of the copper-silicon series. The lowest loss was with 20 per cent. Si. Mr. Smith's Fig. 37 showed the typical structure. This point consists of crystals of primary silicon in the eutectic ε-Si.

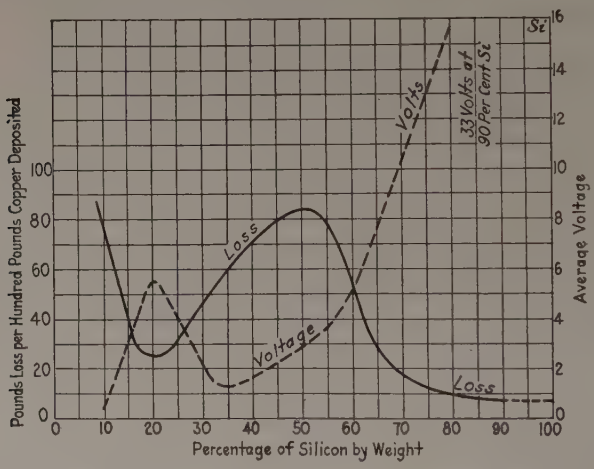


Fig. 39.—Corrosion loss and voltage of copper-silicon series.

M. G. Corson, New York, N. Y. (written discussion).—Mr. Smith says that I peremptorily discarded all previous work as incorrect and suggested a diagram which is very simple, although it does not explain the very marked cooling curve arrests found by the previous workers. He also states that I did not give any experimental details whatever. I presented at the Institute's meeting of February, 1927, a paper that described three binary and four ternary systems of copper alloys, of which a synopsis is given on page 435 of the *Proceedings* of the Institute of Metals Division, 1927. The experimental data concerning copper-silicon alloys which were omitted from that paper on account of lack of space in the volume will be published shortly in a European paper. However, Mr. Smith himself did not introduce any considerable changes in my interpretation of the α range. I believe that the fact that his own investigation resulted in corroborating my diagram in its α part should have convinced Mr. Smith that my interpretation of the diagram had experimental foundation.

[10] C. W. Eichrodt: The Electrolytic Tank House, Chile Exploration Co., Chuquicamata, Chile. *Trans.* Amer. Electrochem. Soc. (1924) **45**.

I made up four alloys containing 7.2, 7.5, 7.8 and 8.1 per cent. silicon, respectively. These were cast in round cylindrical chunks about 200 g. each, with a hole through the center. These chunks were paired with an analogous piece of an alloy containing 3 per cent. silicon and consequently belonging to the α range. In each case the pair was homogenized and heated to 800° in a horizontal tube furnace. A thermocouple was introduced inside each chunk and the temperatures recorded simultaneously both during the heating and cooling. In no case was I able to trace a sharp change in the difference of the temperatures of the two chunks that might indicate any isothermic transformation. That is why I felt it necessary to discard the eutectoid isotherm for the β phase. Two experiments in which I tried to detect isothermic transformation by observing discontinuities in the thermoelectric force generated between a cast rod of a high-silicon alloy and another of a 3 per cent. silicon bronze also failed to produce evidence of such transformation.

Still, I am prepared to grant that a eutectoidal breakdown of the β into α plus δ at 780°, followed by a partial recombination into α plus γ at 720° might correspond to the true nature of the alloys, even though I do not believe much in such complicated processes. I will only stress the results of my examination with the aid of the microscope which showed me clearly that this γ phase has for its high copper limit the composition of 91.9 per cent. copper corresponding to the Cu_5Si compound. I believe this compound to be able to absorb a slight excess of silicon and to represent the true base of the γ phase. Mr. Smith puts this limit at 91.65 per cent. Cu, and this does not differ greatly from the results of my determination.

Finally, about the phase ϵ, which includes the composition corresponding to the compound Cu_3Si and which, according to Mr. Smith, suffers a slight transformation between 620° and 558°, the result of which is a slight decrease of the solubility of silicon in this phase. This interpretation does not explain why this phase is so subject to corrosion instead of forming one of the most corrosion-resistant materials. My own examination of an alloy in this range, as shown in Figs. 13 and 14 of my paper, convinced me that this phase suffers a much more profound transformation, possibly a eutectoidal breakdown. This eutectoidal transformation cannot be made visible when iron chloride etch is used; only a careful application of Vilella's reagent will bring it out.

C. S. Smith (written discussion).—It is much to be regretted that Mr. Corson's paper did not give more complete experimental details, since the possible accuracy of any diagram can only be predicted from the number of points determined. Moreover, it is quite possible even for an experienced worker to misinterpret his experimental facts, but if these are listed subsequent investigators can determine whether the facts themselves agree with their own results and theories.

The sudden reversal in direction of the α phase boundary above 780° C. is so great that I was surprised that Mr. Corson did not observe it, and I could not do other than suppose his experimental points were rather widely spaced, even though his results at lower temperatures are in fair agreement with my own.

As far as the β eutectoidal change is concerned, it is strange that Mr. Corson's cooling curves did not show this, especially as all other workers have detected a change of considerable magnitude at this point. My own work showed this arrest in alloys containing between 6.0 and 8.5 per cent. silicon, the duration of the arrest increasing as the silicon increased up to about 7.8 per cent. and then decreasing rapidly, to disappear at 8.6 per cent. The two cooling curves reproduced in Fig. 40 show the arrest to be quite unmistakable.

As Mr. Corson points out, the γ solid solution can be regarded as the compound Cu_5Si capable of dissolving excess silicon. I had not assigned the compound formula to this constituent, since it is my personal opinion that a constituent should be

regarded as a compound only when a negligibly small range of solubility exists. The fact that a simple atomic ratio usually exists in intermediate solid solutions is due only to the geometrical requirements of the space lattice, and, while I am aware that many well-known metallurgists will not agree with me, I prefer to regard a constituent as an intermetallic compound only when the lattice is so rigid that no solute atoms can enter into it.

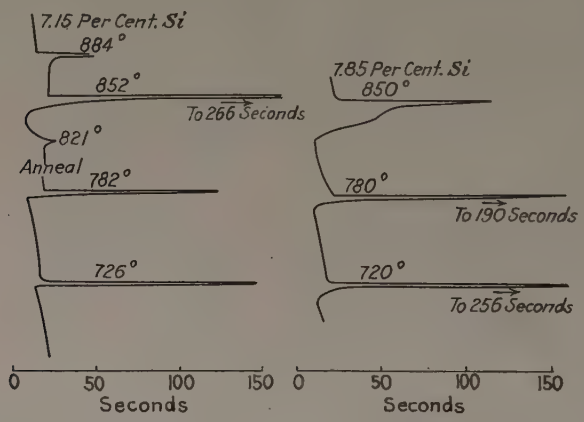


FIG. 40.—INVERSE RATE COOLING CURVES OF TWO β COPPER-SILICON ALLOYS.

As regards the ϵ phase, I can only repeat that my alloys, whatever the etching reagent used, were homogeneous. I still feel that Figs. 30, 31 and 32 in my paper represent the true structure of the alloys, rather than Figs. 13 and 14 in Mr. Corson's paper. It seems fairly certain that a eutectoidal change of the nature suggested by Mr. Corson would be indicated as an unmistakable arrest at constant temperature in the cooling curves.

It does not seem to me to be necessary to assume that copper-silicon alloys should be strongly resistant to corrosion just because iron-silicon or nickel-silicon alloys are.

I will await with interest the publication of Mr. Corson's European paper with the full experimental details.

Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon

By O. W. Ellis,* East Pittsburgh, Pa.

(Philadelphia Meeting, October, 1928)

The question of the influence of gases upon the properties of copper has received the attention of a number of investigators, among whom Sieverts,[1] Iwasé,[2] Lobley and Jepson[3] stand preeminent.

Solubility of Gases in Copper

Sieverts and Iwasé concerned themselves with the solubility of a variety of gases in the metal in the solid and liquid states. They determined the absorption coefficients of these gases and in all cases found a sharp change in solubility at the melting point of the metal. In this respect they disagree with Lobley and Jepson, who have based their opinions upon the appearance of small ingots of the metal which had been fused in an atmosphere of one or other of three gases and had then been rapidly cooled, while surrounded by gas, to the freezing point (rate—possibly 30° to 60° C. per sec.). The ingots that had been fused and cooled under nitrogen and carbon monoxide were free from blowholes and it was assumed that these gases were not absorbed in amounts much in excess of those which would dissolve in the solid metal; the ingots similarly treated under hydrogen were full of blowholes and it was assumed in this case that gas was ejected on solidification of the copper. The effect of varying the rate of freezing upon the character of the test ingots was not examined by these investigators; otherwise, it is felt, their views might have been subject to modification.

Sieverts' most important contribution is that the solubility of a gas in any metal is proportional to the square root of its pressure or concentration. Knowing then the absorption coefficients of the various gases in copper, it should be possible to determine the analysis of the

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[1] A. Sieverts: Zur Kenntnis der Okklusion und Diffusion von Gasen durch Metalle. *Ztsch. phys. Chem.* (1907) **60,** 129.

[2] K. Iwasé: Occlusion of Gases by Metals and Alloys in Liquid and Solid States. *Sci. Repts.* Tohoku Imp. Univ. [1] (1926) **15,** 531.

[3] A. G. Lobley and D. Jepson: Influence of Gases on Copper at High Temperatures. *Jnl.* Inst. Met. (1926) **35,** 213.

gaseous mixture dissolved in molten copper at any temperature, the copper being in equilibrium with an atmosphere of known composition.

The absorption coefficients of carbon monoxide, carbon dioxide, hydrogen and nitrogen are shown in Fig. 1, which is based on the work of Iwasé.

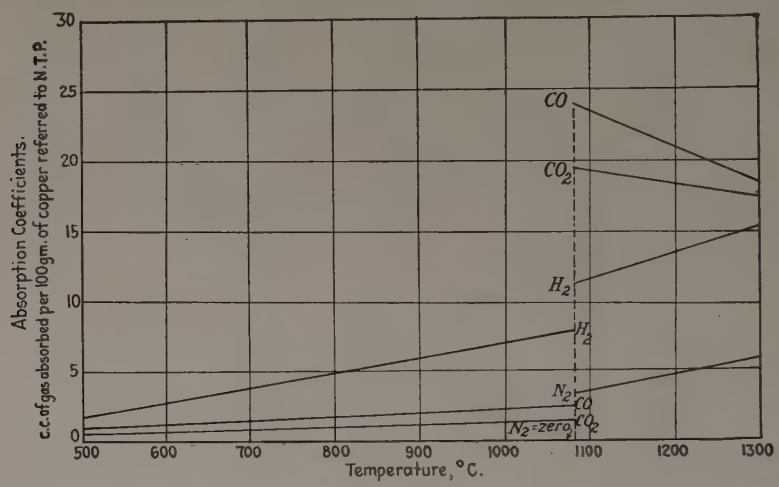

FIG. 1.—ABSORPTION COEFFICIENTS OF CARBON MONOXIDE, CARBON DIOXIDE, HYDROGEN AND NITROGEN. (AFTER IWASÉ.)

SOLUBILITY OF WATER VAPOR IN COPPER

Unfortunately, the information given in Fig. 1 is incomplete, since values for the absorption coefficients of one of the most ubiquitous gases—water vapor—are absent from the diagram. In an endeavor to obtain some idea of the solubility of water vapor in copper, the author

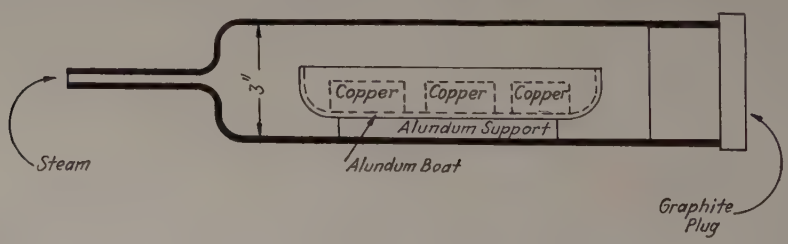

FIG. 2.—ARRANGEMENT OF FURNACE.

performed a very rough experiment, which showed this to be relatively high. Copper was heated, melted, solidified and cooled in an atmosphere of water vapor. The maximum temperature reached was about 1300° C., which was maintained for 20 min. The metal was allowed, after fusion, to cool to a temperature of 500° C., when it was removed from the furnace and immersed in alcohol to prevent surface oxidation. The

cooling from 1300° to 500° C. occupied about one hour. The arrangement of the furnace in which the fusion took place is shown in Fig. 2.

Analysis of the ingot showed it to contain 144.9 per cent. of water vapor, 49.2 per cent. of carbon dioxide, 9.7 per cent. of carbon monoxide and 5.4 per cent. of hydrogen, these percentages being in terms of the volume of the copper.[4] The ingot was full of blowholes. It is almost certain that the carbon monoxide and dioxide resulted from reaction of the water vapor with the graphite plug which was used to seal one end of the furnace, since the metal used had been fused *in vacuo* before it was introduced into the furnace. The copper was free from cuprous oxide before melting but after melting was found to contain oxygen in this form. This oxygen no doubt originated from the dissociation of water vapor ($2H_2O = 2H_2 + O_2$), the hydrogen entering the metal as gas and the oxygen uniting with copper to form cuprous oxide, since no oxygen as gas was found in the copper.

Application of Sieverts' Law to Practice

Even though the absorption coefficients of all the important gases in copper were known it would be impossible to apply Sieverts' law to practice, save with the view of determining the trend of reaction. On the one hand, equilibrium is rarely approached in such furnaces as are in use today or as are likely to find employment in the near future in foundries. On the other hand, the law cannot tell us what will be the gas content in metal which has been poured from the furnace into molds, since the solubility of gases in the solid metal differs materially from their solubility in the melt, despite the apparent contradiction presented in the work of Lobley and Jepson. And again, both the composition and the amount of the gaseous mixture retained in solid copper is dependent on such factors, for example, as the rate of cooling of the metal and the freedom of the copper from cuprous oxide.

Experiments of the Present Investigation

In the author's work copper was melted in the foundry under controlled conditions. Two groups of experiments were performed. In the first (experiments I to IV) the metal was melted in an electric furnace of the indirect arc type; in the second (experiment V) it was fused in an oil-fired furnace of the open-flame barrel type. From the metal small castings were poured, which were (1) examined microscopically, (2) analyzed chemically, and (3) examined for gases.

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[4] All gas volumes mentioned in this article are based on the conditions 1 atm. and 20° C.

Experiment I

The sequence of operations in this experiment was as follows:

a. 250 lb. of scrap copper was raised in temperature to 1250° C.
b. Air was blown through the melt for 20 minutes.
c. The copper was partially skimmed, but not wholly freed from its supernatant layer of slag.
d. Metal was poured as follows:
   1. Direct from the furnace into a small graphite mold 3 in. deep, 2 in. dia. at the top and 1½ in. dia. at the bottom. The ingot (No. 1) occupied only about one-half of the mold, the upper part of the mold being filled with slag. The ingot was completely enveloped in slag and showed no evidence of unsoundness. The chilling effect of the graphite mold may have accounted for the soundness of the ingot.
   2. Direct from the furnace into a large iron ladle and thence into a small graphite mold of the dimensions given. The ingot (No. 2) occupied the entire mold, which contained little, if any, slag. The copper was in direct contact with the mold. The ingot showed no evidence of unsoundness.
   3. Direct from the furnace into a 250-lb. ladle. The metal in the ladle was covered with a heavy layer of slag. Over this a layer of charcoal (briquettes about 1½ in. dia.) was spread. The metal was carried to the molding table and four test ingots were teemed in sand; the first (No. 3) direct from the ladle without any stirring of the melt, the second (No. 4) after adding about 18 oz. of silicon-copper to the melt and thoroughly stirring in, the third (No. 5) after adding a further 18 oz. of silicon-copper and thoroughly stirring it into the melt, and the fourth (No. 6) after again adding 18 oz. of silicon-copper and thoroughly stirring it into the melt. These ingots were about 3 in. long and 1 in. dia. They were invariably unsound.
   4. The remaining metal was poured into chills.

Experiment II

In this experiment 256 lb. of scrap copper was charged. No charcoal was introduced with the metal, nor was any attempt made to exclude air from the interior of the furnace. The metal was first teemed into a ladle, was then covered with a layer of charcoal and was finally carried to the molding table, where six sand ingots (No. 7 to No. 12) were poured. The first ingot was poured direct from the ladle into the mold, no silicon-copper having been added to the melt. The other ingots were poured after successive additions of silicon-copper had been made, as shown in Table 1.

TABLE 1.—*Amounts of Silicon-copper in Ingots 7 to 12*

Casting	Amount of Silicon-copper Added, Oz.	
	Individual	Total
7	nil	nil
8	9	9
9	9	18
10	18	36
11	9	45
12	9	54

All the ingots (3 in. long by 1 in. dia.) showed signs of spewing. The metal, after pouring casting No. 12, was sluggish and was poured into chills.

Experiment III

This experiment consisted of a series of three runs during which no attempt was made to render the furnace airtight, and in which no charcoal was introduced with the charge. In the first run 200 lb. of scrap copper was charged with 56 lb. of oxidized copper (approximately 0.14 per cent. oxygen). In the second run 228 lb. of scrap copper was charged with 28 lb. of oxidized copper. In the third run, 256 lb. of scrap copper alone was charged.

In each case the metal (ingots 13 to 15) was teemed into a ladle containing charcoal and thence into graphite molds of the type already described. No silicon-copper was added to the metal before pouring, nor was the metal found to be of use in the manufacture of castings, since spewing could not be prevented by reasonable additions of silicon-copper.

Experiment IV

In this experiment 256 lb. of scrap copper and 1½ lb. of charcoal was charged. Every precaution was taken to prevent access of air to the interior of the furnace during fusion and superheating of the charge. At the end of the run, a sample of metal was poured into a graphite mold (ingot No. 16). The residue of the metal was then teemed into a ladle, from which three ingots were poured in sand. The metal in the ladle was covered with a layer of charcoal.

The first ingot (No. 17), which was poured from the ladle before any silicon had been added, was unsound. The second ingot (No. 18), poured after 9 oz. of silicon-copper had been thoroughly incorporated in the melt, also showed evidence of spewing. The third ingot (No. 19), poured after a further addition of 9 oz. of silicon-copper, showed no signs of spewing and was found to be quite sound. The metal remaining in the ladle was used successfully in the manufacture of castings.

Experiment V

A series of three runs constituted this experiment, which was conducted in an oil-fired furnace of the type already described. The approximate analysis of the gases in the furnace at the time of making these experiments was: carbon dioxide, 4.0; oxygen, 0.35; hydrogen, 14.5; carbon monoxide, 13.5; methane, 0.35; nitrogen, 67.5 per cent.

The charges involved in this experiment were as follows:

1. 710 lb. of copper wire bar (relatively free from oxide—ingot 20).
2. 710 lb. of scrap copper (relatively free from oxide—ingot 21).
3. 400 lb. of oxidized copper (c. 0.14 per cent. O_2) and 241 lb. of wire bar (ingot 22).

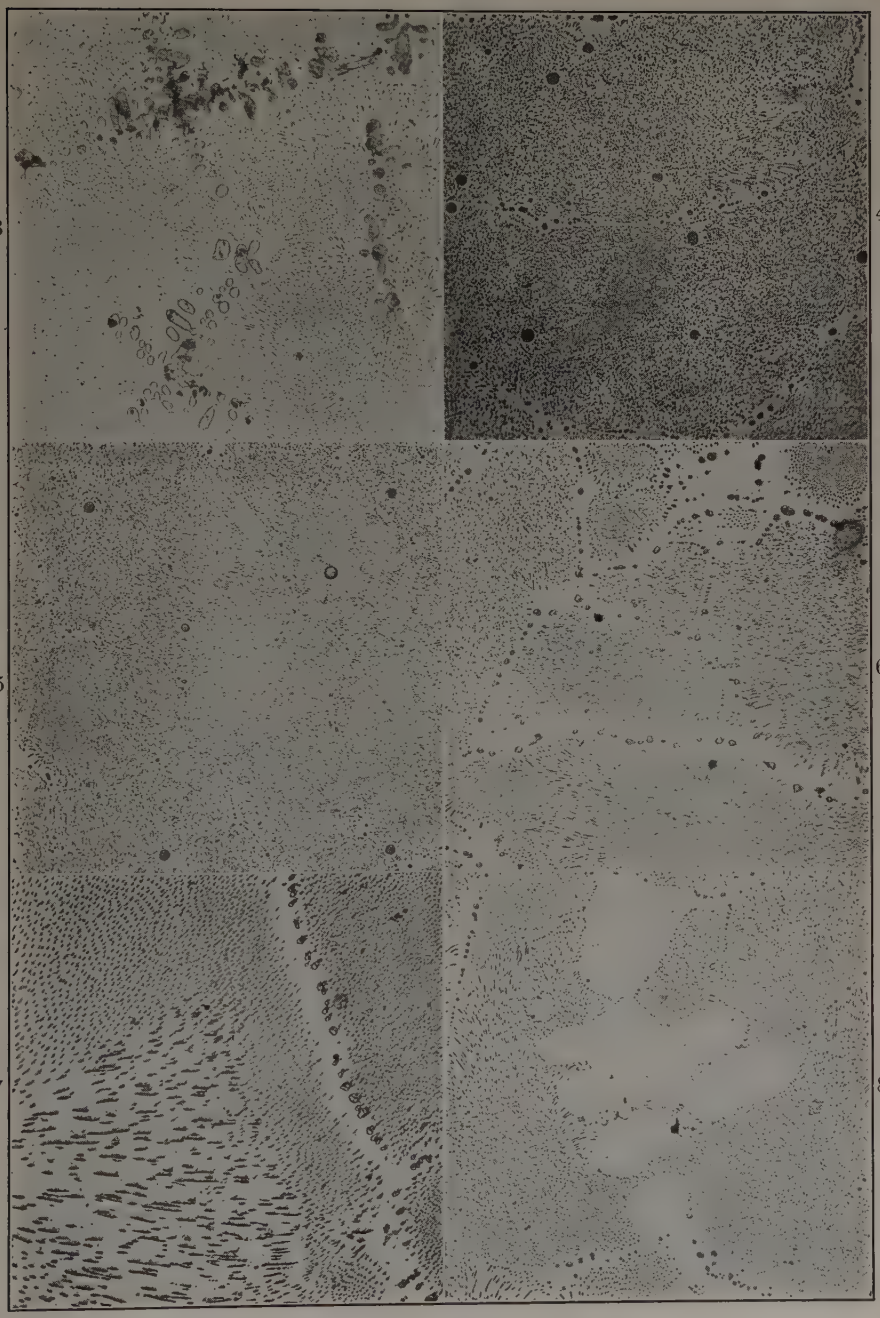
Results of Experiments

Metallographic Examination

From each of the ingots (No. 1 to No. 22) samples were taken for microscopic examination and planimetric measurements were made on all the samples which showed a hypoeutectic cuprous oxide-copper structure. Such measurements cannot be made successfully on hypereutectic alloys; first, on account of the difficulty of measuring the areas occupied by the primary cuprous oxide; and second, because of the uneven distribution of the primary constituent throughout the ingot. Photomicrographs were taken of practically all the samples that contained cuprous oxide in their microstructure.

Experiment I.—Photomicrographs (100 dia.) of the unetched structure of ingots 3, 4 and 5 are shown in Figs. 3, 4 and 5. These cannot be looked upon as representing the structures of the ingots as a whole, since marked segregation of cuprous oxide occurred in all cases. Planimetric measurements were not made on these samples, nor on the sample taken from ingot 6, which had essentially the same structure as that of ingot 5. One important thing brought out by the microscopic examination of these samples was that the addition of silicon-copper to the melt clearly resulted in a reduction of its content of cuprous oxide.

Experiment II.—Photomicrographs (100 dia.) of the unetched structures of ingots 7 to 12 are shown in Figs. 6 to 11. Planimetric measurements of the proportions of primary copper and of eutectic were made on all these samples, an average of three measurements of the areas occupied by these constituents being struck in each case. Ingot 7 was characterized by an almost completely eutectiferous structure. It being assumed that the eutectic of copper and cuprous oxide contained 0.36 per cent. of oxygen, the estimated values for the oxygen content of the ingots shown in Table 2 were obtained. The values quoted in the fourth column of the



FIGS. 3–8.—STRUCTURE OF INGOTS. UNETCHED. × 100.

FIG. 3.—INGOT 3.
FIG. 4.—INGOT 4.
FIG. 5.—INGOT 5.
FIG. 6.—INGOT 7.
FIG. 7.—INGOT 8.
FIG. 8.—INGOT 9.

FIGS. 9–14.—STRUCTURE OF INGOTS. UNETCHED. × 100.

FIG. 9.—INGOT 10.
FIG. 10.—INGOT 11.
FIG. 11.—INGOT 12.
FIG. 12.—INGOT 13.
FIG. 13.—INGOT 14.
FIG. 14.—INGOT 15.

TABLE 2.—*Oxygen Content of Ingots 7 to 12*

Ingot	Silicon-copper Added (Total) Ounces	Oxygen Content	
		Estimated Planimetrically	Calculated from Equation
7	nil	0.36	0.36
8	9	0.33	0.33
9	18	0.31	0.31
10	36	0.29	0.25
11	45	0.24	0.22
12	54	0.18	0.19

table were obtained by subtracting from the first figure, 0.36, the amounts of oxygen that would have been removed from the melt had the silicon added to the copper acted in full accord with the equation:

$$2Cu_2O + Si = SiO_2 + 4\ Cu$$

It will be seen that the silicon has been completely effective in this regard, since the slight differences between the estimated and the calculated

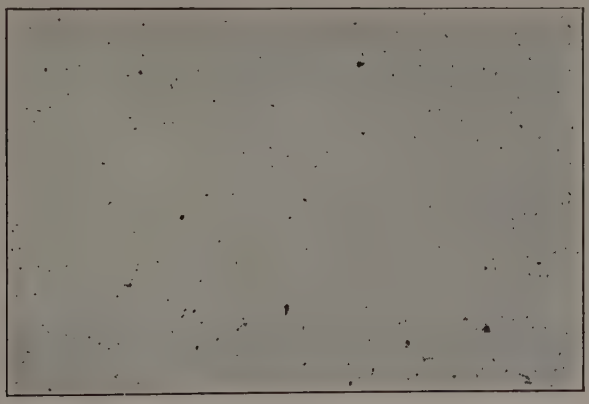


FIG. 15.—STRUCTURE OF INGOT 16. UNETCHED. × 100.

contents of oxygen which are recorded may be assumed to be due to unavoidable experimental errors.

Experiment III.—Photomicrographs of samples from ingots 13, 14 and 15 are shown in Figs. 12 to 14. These make it clear that the amount of cuprous oxide in the copper subsequent to melting depended not only on the oxygen which was absorbed during the fusion and superheating of the metal, but also on the amount of oxygen which was in the metal charged.

Experiment IV.—The structure of ingot No. 16 is shown in Fig. 15, which emphasizes the almost complete absence of cuprous oxide from metal melted in the electric furnace under reducing conditions.

Experiment V.—No photomicrographs of ingots 20 to 22 have been reproduced, since their structure was practically indistinguishable from that shown in Fig. 15.

Chemical Analyses of Ingots

Analyses of the ingots poured were made with the results shown in Tables 3, 4 and 5.

The Gases in Copper

The ingots, after removal of the metallographic and chemical samples, were thoroughly cleaned and were then fused *in vacuo* in a bell-jar furnace of the type described by Brace and Zeigler.[5] The gases extracted from the castings were analyzed in the manner also described in the above paper. The results of these analyses are dealt with in order below:

Experiment I.—Metal Fused in Electric Furnace under Oxidizing Conditions—Air Blown through Melt for 20 Minutes

In Table 6 the gases extracted from the ingots poured in this experiment are tabulated in order of their solubilities in liquid copper at its freezing point (see Fig. 1). There is also quoted the weight of carbon that is present in combination with oxygen in the form of carbon monoxide and dioxide, since this factor appears to be of some importance. No attempt was made to estimate the content of sulfur dioxide.

The outstanding feature of these analyses as a whole is the large volume of gas that has been occluded in the metal. This varies from 105.7 to 366.7 per cent. in terms of the volume of the metal.

Table 3.—*Analyses of Test Ingots of Oxidized Copper**
(R. H. Wynne)

Number of Test Ingot Microstructure Shown in Fig.	7 8	8 9	9 10	10 11	13 12	14 13	15 14
Copper	99.454	99.460	99.462	99.492	99.178	99.252	99.535
Silicon	0.001	trace	0.001	0.002	0.005	0.002	0.002
Tin	0.045	0.024	0.041	0.043	0.033	0.032	0.020
Lead	0.042	0.049	0.044	0.042	0.040	0.049	0.041
Iron	0.006	0.002	0.002	0.004	0.016	0.013	0.011
Zinc	0.027	0.024	0.027	0.028	0.021	0.021	0.063
Sulfur					0.003	0.003	0.004
Insoluble residue	0.012	0.006	0.016	0.017	0.029	0.014	0.008
Balance	0.413	0.435	0.407	0.372	0.675	0.614	0.316

* There is almost as much difficulty in getting a representative sample for chemical analysis from test ingots of hypereutectic copper as there is in getting truly representative photomicrographs.

[5] P. H. Brace and N. A. Ziegler: Application of a High-vacuum Induction Furnace to the Study of Gases in Metals. *Proc.* Inst Metals Div., A. I. M. E. (1928) 544.

TABLE 4.—*Analyses of Test Ingots on Unoxidized Copper**
(R. H. Wynne)

Number of Test Ingot Microstructure as in Fig	17 15	18 15	19 15
Copper	99.290	99.338	99.304
Silicon	0.006	0.001	0.007
Tin	0.132	0.131	0.127
Lead	0.091	0.089	0.092
Iron	0.020	0.003	0.020
Zinc	0.416	0.355	0.419
Sulfur			
Insoluble residue	0.040	0.047	0.028
Balance	0.003	0.036	0.003

* The presence of zinc in this copper can be accounted for only by accidental introduction of zinc into the ladle. The copper behaved in every way as did copper similarly treated in the furnace and ladle on subsequent occasions. It is assumed that the zinc was entirely neutral in its effect on the gas content of the copper.

TABLE 5.—*Analyses of Test Ingots of Copper Melted in the Oil Furnace*
(R. H. Wynne)

Number of Test Ingot Microstructure as in Fig	20 15	21 15	22[a] 15
Copper	99.896	99.802	99.642
Silica	nil	0.001	0.001
Tin	0.028	0.069	0.054
Lead	0.029	0.044	0.084
Iron	0.001	0.006	0.001
Zinc	0.055	0.053	0.217
Sulfur			
Insoluble residue	0.006	0.015	0.012
Balance	negative	0.01	negative

[a] The high zinc content of ingot 22 can be accounted for only by accidental introduction of zinc into the ladle.

It appears from the analyses that the gaseous mixture in the furnace comprised the five gases: oxygen, carbon monoxide, carbon dioxide, nitrogen and water vapor. The almost complete absence of hydrogen from the copper is not surprising in view of the fact that so thorough an oxidation was given the metal while in the furnace.

The more striking features of the above analyses may well be considered in conjunction with Fig. 16. In the first place the general similarity in the analyses of the gases taken from ingot 1, poured direct from the furnace into a graphite mold, contact with which was prevented by a thin but continuous envelope of slag, to those of ingot 3, the first ingot poured in sand, is worthy of note. It is apparent that but little

change in the metal was occasioned by its sojourn in the ladle during its transport from the furnace to the molding table. The most important alteration is in the amount of carbon present in the metal in the form of the gases carbon monoxide and dioxide. In terms of per cent. by weight of total occluded gas the carbon content has increased from 12.9 to 17.9. This increase can be accounted for by reaction between oxide in the melt and the supernatant charcoal. While it is true that the melt was separated from the charcoal by a layer of slag, there is little doubt that the unavoidable jerks and blows given to the ladle on its journey from the furnace to the molding table caused some contact to

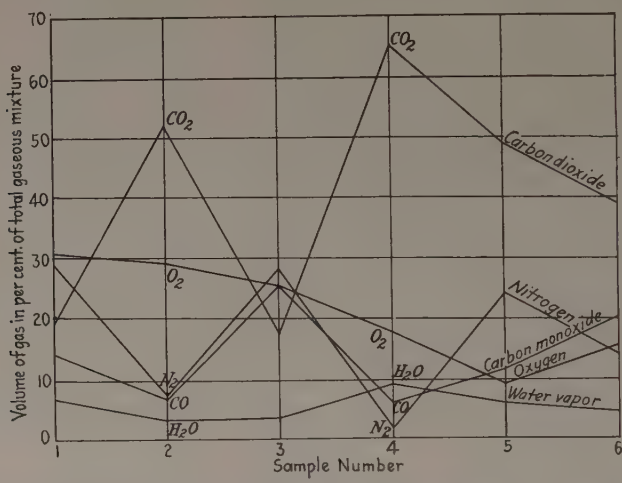


FIG. 16.—CURVES OF GASES EXTRACTED FROM INGOTS POURED FROM METAL FUSED IN THE ELECTRIC FURNACE UNDER OXIDIZING CONDITIONS, WITH AIR BLOWN THROUGH THE MELT FOR TWENTY MINUTES.

be made between the melt and the charcoal. As a result of this contact, the gaseous carbon content of the melt increased. A study of the analyses recorded in Table 6 leads to the view that oxidized copper can and will absorb carbon up to a limit of about 21.9 per cent. by weight of total occluded gas. This carbon is distributed between the two gases carbon monoxide and carbon dioxide in proportions which are dependent only on the temperature. The higher the temperature of the oxidized melt when saturated with carbon, the greater is the proportion of carbon dioxide occluded. This is a result that would be foreseen from a study of the absorption coefficients of carbon monoxide and carbon dioxide in liquid copper at various temperatures (Fig. 1).

It then appears that the copper in this experiment, during its transportation from the furnace to the molding table, has been enabled to absorb, but not to saturate itself with, carbon. At the same time, its temperature having fallen, the ratio CO to CO_2 in the metal has increased.

For the same reason that this ratio has altered, the proportions of oxygen, nitrogen and water vapor have diminished.

In the second place, the surprising difference in the proportion of carbon dioxide in ingots 1 and 2 claims some attention. It will be remembered that in casting ingot 1 the metal was poured into a graphite mold from which it was protected by a continuous layer of slag. Absorption of carbon from the mold by the copper was thereby largely, if not entirely, prevented. In casting ingot 2 the metal was poured into a large iron ladle and thence into a graphite mold, with which the hot copper made intimate contact. The copper absorbed much carbon, though it did not become saturated with the element. Its CO/CO_2 ratio was, however, depressed towards the normal value for the temperature in question.

A third point of interest is the remarkable increase in the proportion of carbon dioxide in ingot 4. This ingot was poured from the ladle into a sand mold at the molding table after 18 oz. of silicon-copper had been added to the melt. The silicon-copper was stirred into the metal so vigorously that no question can arise as to the opportunity given the copper and its solutes to react with both the silicon and the charcoal of the cover. From the latter the maximum weight of carbon was absorbed and united with oxygen in the melt, forming carbon monoxide and dioxide. The total carbon present in ingot 3, poured prior to the first addition of silicon-copper, was 17.9 per cent.; that present in ingot 4 was 21.9 per cent. This represents an increase in carbon of 4.0 per cent.

The difference in the carbon dioxide content in ingots 3 and 4—49.1 per cent.—could be accounted for by the following reactions:

$$2CO + O_2 = 2CO_2 \qquad (1)$$
$$C + O_2 = CO_2 \qquad (2)$$

As a result of the first reaction, the carbon monoxide is reduced from 26.1 per cent. by weight (ingot 3, Table 6) to 4.4 per cent. by weight (ingot 4, Table 6)—a reduction of 21.7 per cent. by weight. The reaction of this 21.7 per cent. of carbon monoxide with oxygen (equation 1) results in the formation of 34.3 per cent. of carbon dioxide.

As a result of the second reaction, 4.0 per cent. of carbon (carbon content of ingot 4 minus carbon content of ingot 3) produces 14.8 per cent. of carbon dioxide. The sum of 34.3 and 14.8 should give the total increase in carbon dioxide, 49.1 per cent.

This increase in carbon dioxide involves a percentage weight of 23.0 per cent. of oxygen. But only 1.6 per cent. of gaseous oxygen is lost by the copper, hence either oxygen resulting from the reduction of cuprous oxide or oxygen from the air must have assisted in bringing these reactions to completion. That oxygen from the air could get into the copper is certain in view of the conditions under which the silicon was incorporated with the melt.

It appears then that copper can become saturated with carbon only if and when sufficient gaseous oxygen is available. In view, also, of the fact that the ratio of carbon monoxide to carbon dioxide in oxidized copper saturated with carbon varies with temperature, the proportion of gaseous oxygen combined with carbon must vary too.

The subsequent additions of silicon-copper (ingots 5 and 6) were followed by vigorous stirring of the melt in the ladle and as a result the limiting amount of carbon was absorbed by the copper. The distribution of the carbon varied in accordance with the amount of oxygen combined with it, which became less as the temperature of the melt decreased; or, in other words, as the time the melt remained in the ladle lengthened.

In passing on to the last point, attention may be directed to the fact that the content of gaseous oxygen falls uniformly until the last ingot (No. 6) is reached. The fact that the metal was sluggish in the ladle and that some separation of primary copper had probably already supervened may account for the increase in oxygen noted in the last ingot.

The last observation is that silicon-copper appears to act as a deoxidizer in complete accordance with the equation:

$$2Cu_2O + Si = SiO_2 + 4Cu \qquad (3)$$

The metal capacity of the ladles used in this and the subsequent experiments was 225 lb. In a melt of such capacity a cuprous oxide content of 1 per cent. would be equivalent to 2¼ lb. of cuprous oxide, or a little over 4 oz. of oxygen (as cuprous oxide). To reduce this amount of cuprous oxide, almost exactly 2¼ lb. of 10 per cent. silicon-copper would be required. The conclusion is reached, then, that 1 oz. of 10 per cent. silicon-copper added to a 225-lb. ladle of oxidized copper should reduce 0.028 per cent. of cuprous oxide to copper and that the usual 9-oz. piece of silicon-copper used in these experiments should reduce 0.252 per cent. of cuprous oxide to copper or, in other words, react with 0.028 per cent. of oxygen in the form of cuprous oxide to form silica (SiO_2) which, owing to its inferior density (2.2), will gravitate from the melt.

The evidence in support of the contention that silicon-copper acts as a deoxidizer in complete accordance with equation 3 is based upon the results of experiment II, rather than on the results just described. In the experiment now under discussion planimetric measurements of the oxide content of samples 3 to 6 were vitiated by the fact that the alloys were so heterogeneous in structure. Accurate determinations of the oxide content could only have been made had the whole cross-sectional areas of the castings been the subjects of measurement. In the case of hypoeutectic alloys this difficulty is not encountered, since the distribution of the microconstituents is generally uniform over the entire cross-section of the ingots.

TABLE 6.—*Solubilities of Gases in Copper under Oxidizing Conditions*

Ingot Number	Gas	Weight of Gas in Per Cent. of		Volume of Gas in Per Cent. of	
		Copper	Total Gas	Copper	Total Gas
		Experiment I			
1	O_2	0.00928	31.3	57.5	30.8
	CO	0.00380	12.9	26.9	14.4
	CO_2	0.00800	27.2	35.4	19.0
	H_2	nil	nil	nil	nil
	N_2	0.00743	25.1	54.0	29.0
	H_2O	0.00103	3.5	12.5	6.8
	Carbon		12.9		
	Total			186.3	
2	O_2	0.01610	24.9	99.7	29.2
	CO	0.00340	5.3	24.0	7.0
	CO_2	0.04000	62.1	178.0	52.1
	H_2	0.00003	0.4	2.7	0.8
	N_2	0.00353	5.5	25.9	7.6
	H_2O	0.00115	12.1	11.2	3.3
	Carbon		19.3		
	Total			341.5	
3	O_2	0.00810	17.6	93.2	25.4
	CO	0.01200	26.1	93.2	25.4
	CO_2	0.01140	24.7	64.5	17.6
	H_2	nil	nil	nil	nil
	N_2	0.01360	29.5	103.0	28.1
	H_2O	0.00095	2.1	12.8	3.5
	Carbon		17.9		
	Total			366.7	
4	O_2	0.00320	16.0	18.8	17.8
	CO	0.00088	4.4	6.2	5.9
	CO_2	0.01490	73.8	69.0	65.3
	H_2	nil	nil	nil	nil
	N_2	0.00027	1.3	2.0	1.8
	H_2O	0.00089	4.5	9.7	9.2
	Carbon		21.9		
	Total			105.7	
5	O_2	0.00352	8.3	22.0	9.1
	CO	0.00393	9.3	28.0	11.7
	CO_2	0.02610	61.4	117.0	48.9
	H_2	nil	nil	nil	nil
	N_2	0.00790	18.5	58.2	24.3
	H_2O	0.00109	2.5	14.4	6.0
	Carbon		20.8		
	Total			239.6	
6	O_2	0.00354	15.1	22.1	15.6
	CO	0.00416	17.6	28.5	20.4
	CO_2	0.01240	52.6	55.3	39.0
	H_2	0.00010	0.4	9.4	6.4
	N_2	0.00278	11.9	20.2	14.2
	H_2O	0.00057	2.4	6.3	4.4
	Carbon		21.8		
	Total			141.8	
		Experiment II			
7	O_2	0.00126	6.5	7.7	6.5
	CO	0.00048	2.5	3.4	2.8
	CO_2	0.01157	59.5	55.0	45.9
	H_2	0.00003	0.6	3.3	2.8
	N_2	0.00446	22.9	32.5	27.2
	H_2O	0.00163	8.4	17.7	14.8
	Carbon		17.3		
	Total			119.6	
8	O_2	0.00187	10.1	11.5	10.3
	CO	0.00336	18.1	23.6	21.1
	CO_2	0.01039	55.9	46.0	41.1
	H_2	0.00005	0.3	4.7	4.2
	N_2	0.00142	7.6	9.8	8.8
	H_2O	0.00149	8.0	16.2	14.5
	Carbon		23.0		
	Total			118.8	
9	O_2	0.00253	6.8	15.5	7.6
	CO	0.00400	10.6	28.3	13.9
	CO_2	0.02650	70.7	117.9	57.6
	H_2	0.00002	0.1	1.6	0.8
	N_2	0.00305	8.1	24.8	12.1
	H_2O	0.00150	4.0	16.4	8.0
	Carbon		23.7		
	Total			204.1	
10	O_2	0.00018	0.8	1.1	0.7
	CO	0.00379	16.6	26.6	16.8
	CO_2	0.01305	57.0	65.8	42.3

TABLE 6.—(*Continued*)

Ingot Number	Gas	Weight of Gas in Per Cent. of		Volume of Gas in Per Cent. of	
		Copper	Total Gas	Copper	Total Gas
	H_2	0.00009	0.4	8.8	5.6
	N_2	0.00230	10.1	16.9	10.8
	H_2O	0.00339	14.8	37.0	23.8
	Carbon		22.6		
	Total			156.2	
11	O_2	nil	nil	nil	nil
	CO	0.00845	13.8	59.6	18.5
	CO_2	0.04990	81.2	221.0	68.3
	H_2	0.00011	0.2	10.4	3.2
	N_2	nil	nil	nil	nil
	H_2O	0.00298	4.8	32.3	10.0
	Carbon		28.0		
	Total			323.3	
12	O_2	nil	nil	nil	nil
	CO	0.00309	12.9	21.8	17.4
	CO_2	0.01488	62.1	45.6	36.5
	H_2	0.00008	0.3	6.7	5.2
	N_2	0.00362	15.1	26.3	21.1
	H_2O	0.00229	9.6	24.8	19.8
	Carbon		22.4		
	Total			125.2	
		Experiment III			
13	O_2	0.00052	3.6	3.2	4.1
	CO	0.00014	1.0	1.0	1.3
	CO_2	0.01140	78.9	50.4	65.1
	H_2	0.00001	0.1	0.7	0.8
	N_2	0.00095	6.6	6.9	8.9
	H_2O	0.00142	9.8	15.3	19.8
	Carbon		21.9		
	Total			77.5	
14	O_2	0.00084	13.8	5.2	11.5
	CO	0.00085	14.0	6.0	13.4
	CO_2	0.00362	55.0	16.1	35.5
	H_2	0.00005	0.1	4.5	10.0
	N_2	nil	nil	nil	nil
	H_2O	0.00122	18.6	13.4	29.6
	Carbon		21.0		
	Total			45.2	
15	O_2	0.00082	12.4	5.0	13.6
	CO	nil	nil	nil	nil
	CO_2	0.00484	73.1	21.5	58.2
	H_2	nil	nil	nil	nil
	N_2	nil	nil	nil	nil
	H_2O	0.00095	14.4	10.4	28.2
	Carbon		19.9		
	Total			36.9	

Experiment II.—Metal Fused in Electric Furnace under Oxidizing Conditions

The results of the analyses of the gases extracted from the ingots poured in experiment II are shown in Table 6 and, with the exception of that of ingot 11, in Fig. 17. The analysis quoted for ingot 11 is undoubtedly incorrect. At the conclusion of this analysis the refractories used were found to be covered with a deposit of what appeared to be iron oxide. It was clear that the refractories had not been thoroughly cleansed before introduction into the furnace. The abnormal values—in particular those for carbon dioxide—can be accounted for only on this basis. It is interesting to note that the weight of carbon in per cent. of occluded gas is far above the average value (21.9 per cent.) contained in the 10 ingots where ample opportunity was given

the oxidized melt to make contact with carbon; *viz.*, Nos. 4, 5, 6, 8, 9, 10, 11, 12, 13, 14 and 15.

Granting that the views given in this paper regarding the absorption of carbon by oxidized copper are correct, it would appear that in ingot 7 the low carbon content is to be accounted for by the fact that, although some contact between the melt and the cover occurred during the transport of the copper from the furnace to the molding table, the metal did not become saturated with carbon. However, when opportunity had been given the melt to react with the cover, as it did when the first addition of silicon-copper was being incorporated (ingot 8), its carbon content rose to 23.0 per cent., a value slightly above the average.

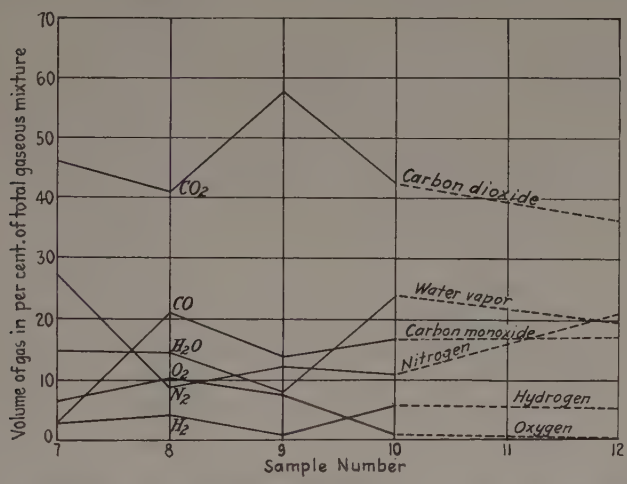


FIG. 17.—CURVES OF GASES EXTRACTED FROM INGOTS POURED FROM METAL FUSED IN THE ELECTRIC FURNACE UNDER OXIDIZING CONDITIONS.

The analyses quoted in Table 6 and shown in Fig. 17 do not fall in line with the writer's views in regard to the effect of temperature on the CO_2/CO ratio. His hypothesis would call for a carbon dioxide content (volume) greater than 57.6 per cent. in ingot 8 (*i. e.*, a carbon dioxide greater than that in ingot 9) for the reason that the temperature of the metal when this ingot was poured was greater than that when the succeeding ingots were poured. The trend of the gas analyses for ingots 9, 10 and 12 quite fall in line with the writer's theory; *viz.*, that the CO_2/CO ratio of oxidized copper saturated with carbon falls with fall of temperature. It is most unfortunate that the analysis of ingot 11 was a failure, since it might have afforded useful evidence in this connection.

It will be noted (Fig. 17) that there is a uniform fall in oxygen (gaseous) content with increase of silicon. It may be concluded from this experiment:

1. That silicon acts as a deoxidizer in complete agreement with the stoichiometric requirements of the equation:

$$2Cu_2O + Si = 4Cu + SiO_2$$

2. That silicon also removes gaseous oxygen from copper.

3. That when given opportunity oxidized copper can become saturated with carbon.

Experiment III.—Metal Fused in Electric Furnace under Oxidizing Conditions

The planimetric analyses of the samples dealt with in this experiment gave the following results: ingot 13, 0.92 per cent. oxygen; ingot 14, 0.87 per cent. oxygen; ingot 15, 0.22 per cent. oxygen.

Ingots 13 and 14 exhibited a hypereutectic structure and there can be little doubt, therefore, that the first two results are high. There can be no question, however, as to the oxygen content of ingot 15.

The gas analyses of these ingots are quoted in Table 6. These analyses serve to confirm the view that oxidized copper can, when given opportunity, absorb carbon in amounts up to about 21.9 per cent. of this element in terms of the weight of gas per cent. of total occluded gas.

No determinations of the temperature of the melts were made at the time of pouring. It is of interest to note, however, that 100 kw.-hr. were expended in the fusion and superheating of the metal from which ingots 13 and 15 were poured, while somewhat less energy—about 80 kw.-hr.—was used in melting the charge for ingot 14. In view of the fact that the conditions under which the runs were made were otherwise almost identical, it may be concluded that the temperature of the melt at the time of pouring ingot 14 was less than that of the melts at the time of pouring the other two castings. It is not surprising, then, to find that the CO_2/CO ratio in the case of ingot 14 is less than that in the case of ingots 13 and 15. We may also conclude that not more than about 80.5 per cent. by weight of total occluded gas in oxidized copper can be carbon dioxide. Variations in the water vapor content of the metal, however, will have an effect on this percentage.

A point in connection with these experiments seems worthy of note; *viz.*, that the total gas content of the ingots from these three runs varies directly as the amount of oxide in the ingots. It may be assumed that the pressure of the gaseous mixture in the furnace during these three runs was the same. Hence it might be expected that, other things being equal, the amount of gas that would be retained in the copper would be the same in all cases. Of course it must be remembered that strictly comparable conditions are hard to obtain in such experiments as these, and further, that it is assumed that the gas content of the ingot is representative of the gas content of the melt! It is possible, however, that the amount

of oxide which separates from a melt during cooling may have an important effect upon the total quantity of gas (not necessarily upon the composition of the gaseous mixture) occluded by the solid metals. If the particles of oxide are considered as nuclei upon which gas may be absorbed, then the fact that ingot 13 contains more gas than either ingot 14 or 15 may be explained on the assumption that the amount of oxide upon which gas could be adsorbed was greatest in the case of the first casting.

It may be noted that, on the whole, the total amount of gas was greatest in the case of the ingots poured from metal that had been aerated (experiment I) and was least in the case of the ingots which were made from metal practically free from oxide (see experiment IV). The amount of gas was relatively high in the case of ingots made from oxide-free metal melted in the oil furnace (see experiment V), but the pressure of gas in the oil furnace was, of course, greater than atmospheric and the amount of gas absorbed by the molten copper would, therefore, be relatively higher.

Experiment IV.—Metal Fused in Electric Furnace under Reducing Conditions

In this experiment every precaution was taken to exclude air from the furnace during the runs. The ingots were found to contain gaseous oxygen but were practically free from cuprous oxide. The analyses of the gases are quoted in Table 7 and are chiefly of interest for two reasons:

1. The relatively small amount of gas retained in the ingots.
2. The virtual absence of carbon monoxide from the gaseous mixture extracted from the castings.

Ingot 16 was poured direct from the furnace into a graphite mold; ingot 17 was poured from a ladle, which had been carried from the furnace to the molding table, into a sand mold. The metal was covered with charcoal during its journey from the furnace to the molding table. There was little change in the weights of carbon dioxide and oxygen in the metal during the time that was occupied in the transport of the metal from the furnace to the table. There was, however, a marked change in the relative proportions of nitrogen and water vapor, the latter having increased at the expense of the former.

The addition of 9 oz. of silicon-copper (ingot 18) has altered the distribution of the gases in the copper. Both the carbon dioxide and the oxygen have increased at the expense of the nitrogen. The vigorous stirring of the melt may be credited with having caused the increase in these two gases. The silicon-copper may have been acting upon cuprous oxide only. If this assumption be made, the remarkable effect of adding a further 18 oz. of silicon-copper (ingot 19) to the melt can be explained on the assumption that in this case the silicon-copper has acted upon the gaseous oxygen and the carbon dioxide and has reduced them to pro-

TABLE 7.—*Solubilities of Gases in Copper under Reducing Conditions*

Ingot Number	Gas	Weight of Gas in Per Cent. of		Volume of Gas in Per Cent. of	
		Copper	Total Gas	Copper	Total Gas
16	O_2	0.00010	3.0	0.8	2.5
	CO	nil	nil	nil	nil
	CO_2	0.00149	44.0	14.1	44.8
	H_2	nil	nil	nil	nil
	N_2	0.00100	30.0	7.5	23.8
	H_2O	0.00080	23.6	9.1	28.9
	Carbon		12.0		
	Total			31.5	
17	O_2	0.00014	4.3	0.9	0.4
	CO	0.00005	0.1	0.3	0.1
	CO_2	0.00149	44.2	6.6	31.8
	H_2	nil	nil	nil	nil
	N_2	0.00151	44.9	10.9	52.6
	H_2O	0.00018	5.3	2.0	15.1
	Carbon		12.0		
	Total			26.2	
18	O_2	0.00080	17.6	4.9	18.7
	CO	nil	nil	nil	nil
	CO_2	0.00248	54.3	11.0	42.0
	H_2	nil	nil	nil	nil
	N_2	0.00103	22.6	7.5	28.6
	H_2O	0.00026	5.7	2.8	10.7
	Carbon		14.8		
	Total			26.2	
19	O_2	0.00032	5.2	2.8	6.9
	CO	nil	nil	nil	nil
	CO_2	0.00200	32.7	8.9	2.0
	H_2	nil	nil	nil	nil
	N_2	0.00330	54.0	24.1	59.5
	H_2O	0.00050	8.4	4.7	11.6
	Carbon		8.9		
	Total			40.5	

portions below those which will cause trouble due to unsoundness in the casting, sound castings having been obtained subsequent to the addition of 18 oz. of silicon copper.

It is certainly difficult to give an entirely rational explanation of these analyses. Much further work requires to be done before the true action of silicon-copper in this connection can be arrived at. That it acts as a deoxidizer is certain, but whether or not its ability to promote soundness lies in this action alone is a debatable question.

Experiment V.—Metal Fused in Oil Furnace

The analyses of the gases extracted from the ingots (No. 20 to 22) poured from these melts are quoted in Table 8.

It should be noted that after the ingots had been poured the ladle in each case was taken to the molding table where, after addition of silicon-copper (not more than 18 oz.) to the melt, a number of perfectly sound sand castings were poured.

TABLE 8.—*Solubilities of Gases in Copper Fused in Oil Furnace*

Ingot Number	Gas	Weight of Gas in Per Cent. of		Volume of Gas in Per Cent. of	
		Copper	Total Gas	Copper	Total Gas
20	O_2	0.00040	2.7	2.5	2.9
	CO	0.00126	8.4	8.9	10.4
	CO_2	0.01120	5.0	50.0	58.1
	H_2	0.00004	0.3	3.6	4.2
	N_2	0.00050	3.3	4.0	4.7
	H_2O	0.00155	10.4	16.9	19.7
	Carbon		24.0		
	Total			85.9	
21	O_2	0.00021	1.8	1.3	1.9
	CO	0.00153	13.1	10.8	16.2
	CO_2	0.00850	72.5	37.8	56.6
	H_2	0.00003	0.2	3.0	4.5
	N_2	0.00046	3.9	3.3	4.9
	H_2O	0.00100	8.5	10.6	15.9
	Carbon		25.3		
	Total			66.8	
22	O_2	nil	nil	nil	nil
	CO	0.00257	21.5	18.1	21.2
	CO_2	0.00828	69.2	36.6	43.1
	H_2	0.00021	1.8	20.3	23.9
	N_2	nil	nil	nil	nil
	H_2O	0.00091	7.6	10.0	11.8
	Carbon		28.0		
	Total			85.0	

In these ingots, 20 to 22, the amount of carbon absorbed by the metal was relatively high (24.0 to 28.0 per cent.) as compared with the 8.9 to 14.8 per cent. found in the metal melted under reducing conditions in the electric furnace. Some of this carbon is present as carbon monoxide. In this respect, also, the gases absorbed by the copper in oil-furnace practice differ from those absorbed by the metal electric-furnace practice.

Other features of the analyses are (1) the presence of hydrogen in the extracted gases, and (2) the marked difference between the hydrogen content of the ingots poured from metal which, prior to melting, was practically free from oxide and metal which had been definitely oxidized.

Yet another point seems worthy of note. If the ingots be arranged, as in Table 8, in the order of the oxide content (increasing) of the charges from which they were poured, it will be noted that their content of carbon monoxide increases, while that of carbon dioxide decreases. The question then arises as to whether the increase in carbon monoxide may be accounted for by assuming some reaction of the following nature to occur during fusion of the charge:

$$CH_4 + Cu_2O = 2Cu + 2H_2 + CO \qquad (4)$$

It is of interest to note that the hydrogen content is higher in the ingots poured from the initially oxidized copper, which is what might be expected on the above assumption.

Validity of Assumptions

The question arises as to how far the analysis of the gases extracted from a casting can be taken to represent the analysis of the gases in the melt; in other words, to what extent is the high-temperature equilibrium frozen in the cold metal by rapid cooling? That it is partly congealed is shown by the fact that nitrogen, which is insoluble in solid copper under conditions of equilibrium, is always present in ingots and castings of the type under consideration in this paper. While fully recognizing the fact that the high-temperature equilibrium of gases in copper can only be partly congealed in the solid state, the writer believes that the analyses quoted in Tables 6, 7 and 8 may justly form the basis of such a discussion as is presented in this paper, a discussion which, it is hoped, may prove the starting point of other work in this connection.

The author bases his belief upon the results of two experiments in which both the gas occluded in the copper after solidification and the gas given off during the cooling of the metal from the liquid state were analyzed.

In these experiments copper was poured from a ladle into an open sand mold 4 in. in diameter and 8 in. deep. Into the still molten copper a silica tube connected with an evacuated bulb in the manner shown in Fig. 18 was introduced. While the tube was being lowered into the copper the stopcock *A*, through which heated air and gas could escape from the silica tube, was allowed to remain open. The tube was lowered into the metal until a volume of approximately 100 c. c. of the tube was still unfilled with metal. The stopcock *A* was closed 15 sec. after the silica tube had reached its lowest position relative to the molten copper. During this time, it was assumed that most, if not all, of the air originally in the silica tube would have been displaced by gases evolved from the metal.

After a further wait of one minute, stopcock *B* was opened and the gases above the copper distributed themselves between the container and the bulb. Stopcock *B* was allowed to remain open for 4 min. before closing. The bulb was later separated from the container by melting the Khotinsky cement which connected them.

The results of the analyses of the gases collected in the bulb and extracted from the ingot are quoted in Table 9.

The metal used in pouring the castings in these two experiments had been melted in an oil furnace. That used in the first experiment was from a charge that consisted entirely of copper scrap; that used in the second experiment was from a charge which consisted in part of oxidized copper (about 0.14 per cent. oxygen).

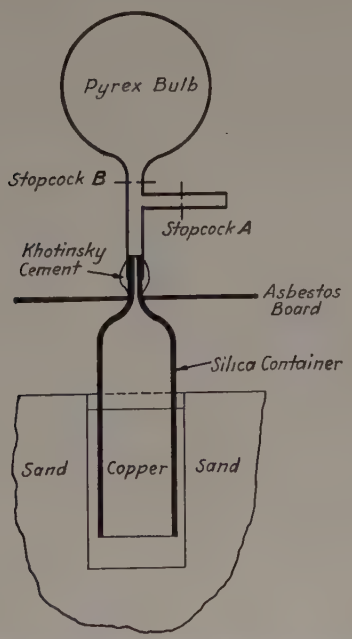


FIG. 18.—APPARATUS USED IN MOLDING TEST INGOT AND COLLECTING GASES GIVEN OFF DURING THE COOLING OF THE METAL.

The analyses in Table 9 may be compared with those given in Table 8, which refer to the gases extracted from test ingots (3 in. long by 1 in. dia.) made from metal similarly melted. The analysis of the gases in experiment A (Table 9) may be compared with those of the gases extracted from ingots 20 and 21 (Table 8); those of the gases in experiment B may be compared with those of the gases extracted from ingot 22.

The first point of interest is the fact that the volume of gas (per cent. of copper) occluded in the test ingots 20, 21 and 22 is of the same order as the total volume of gas evolved from and occluded in the castings dealt with in experiments A and B (Table 9).

TABLE 9.—*Analyses of Gas Evolved and Extracted from Test Ingots of Copper*

Gases, etc., Obtained on Analysis	Weight of Gas (Per Cent. of Copper)		Weight of Gas (Per Cent. of Gas)		Volume of Gas (Per Cent. of Copper)		Volume of Gas (Per Cent. of Gas)	
	Evolved	Occluded	Evolved	Occluded	Evolved	Occluded	Evolved	Occluded
	(Experiment A—scrap copper)							
Water vapor	0.00013	0.00189	2.4	30.5	1.6	21.0	3.9	47.4
Hydrogen	0.00002	nil	0.4	nil	1.9	nil	4.6	nil
Carbon monoxide	0.00017	0.00135	3.1	22.1	1.2	9.6	2.9	21.6
Carbon dioxide	0.00026	0.00259	4.8	42.0	1.1	11.6	2.7	26.2
Nitrogen	0.00462	0.00003	84.5	0.5	33.8	0.2	81.9	0.5
Oxygen	0.00026	0.00030	4.8	4.9	1.6	1.9	3.9	4.2
Carbon				20.9				
Total					41.1	44.3		
	(Experiment B—oxidized copper)							
Water vapor	0.00008	0.00142	3.1	14.9	0.9	15.5	5.5	24.9
Hydrogen	nil	0.00010	nil	1.1	nil	10.1	nil	16.3
Carbon monoxide	0.00005	0.00038	1.9	4.0	0.4	2.7	2.2	4.3
Carbon dioxide	0.00018	0.00760	4.2	79.7	0.5	33.8	2.8	54.2
Nitrogen	0.00140	nil	53.4	nil	10.2	nil	56.0	nil
Oxygen	0.00098	0.00003	37.4	0.3	6.1	0.2	33.5	0.8
Carbon				2.34				
Total					18.1	62.3		

The second point of interest is that the same gases were occluded in the copper of experiment A (Table 9), made from copper which was oxygen-free when charged into the Schwartz furnace, as were occluded in ingots 20 and 21, similarly made. Low hydrogen content and presence of nitrogen characterize these castings. On the other hand, the copper of experiment B (Table 9), made from metal which was oxidized when charged, is characterized by the absence of nitrogen and by a high content of hydrogen, in this respect being similar to ingot 22.

The most important fact, however, is that even on slow cooling a fairly large casting the amount of gas evolved, as compared with that occluded, is relatively small, if nitrogen and oxygen be excepted. The proportions which were evolved on cooling the casting in experiments A and B are shown in Table 10.

TABLE 10.—*Gases Evolved on Cooling Casting*

Percentage of Gas Evolved, *i. e.* $\left(\frac{\text{Gas evolved} \times 100}{\text{Gas evolved} + \text{Gas occluded}}\right)$

	A	B
Water vapor	7.1	5.5
Hydrogen	all	nil
Carbon monoxide	11.1	12.9
Carbon dioxide	8.7	1.46
Nitrogen	practically all	all
Oxygen	45.7	97.0

Now the rate of cooling of test ingots such as those dealt with in this paper must be very rapid as compared with that of the castings referred to in Table 9. The rate of cooling was, in fact, so rapid that the test ingots quite frequently contained nitrogen. It is maintained, therefore, that the analyses discussed above represent with a fair degree of accuracy, in so far as the gases other than nitrogen are concerned, the analyses of the gases which were contained in the liquid metal at the time it was poured into the test molds.[6] On this account some justification exists for the conclusions arrived at above and recapitulated below.

Conclusions

It is clear that much remains to be done in this connection. The complexity of the problem is evident, but the following conclusions stand out preeminently:

1. The total volume of gas occluded by solid copper is, other things being equal, a function of the conditions under which it is melted. This fact is well recognized, but is frequently overlooked when the question of occluded gases is under discussion. It is fully realized by the writer that the total volume of gas occluded by solid copper is a function *also* of the rate of cooling of the metal.

2. Oxidized copper, when brought into contact with carbon, absorbs this element up to a certain fairly well defined limit, the carbon distributing itself between the gases carbon dioxide and carbon monoxide in proportions which are dependent on the temperature of the metal.

3. Very little carbon (1½ lb. charcoal per 150-lb. charge) suffices to prevent the oxidation of copper in electric furnace melting practice, when precautions are taken to prevent undue access of air to the interior of the furnace.

4. Castings made from copper melted under reducing conditions in the electric furnace contain neither hydrogen nor carbon monoxide; carbon dioxide, nitrogen and water vapor are the principal constituents of the gaseous mixture in castings made from such metal.

5. Conditions in the oil-fired furnace may be made so reducing as to remove practically all traces of cuprous oxide from oxidized copper charged and melted therein. It is worthy of note, however, that zinc oxide in brass is not reduced under like conditions.

6. Nitrogen is practically absent in copper melted in the oil-fired furnace; carbon dioxide, carbon monoxide and water vapor are the principal constituents of the gaseous mixture in castings made from such metal.

7. Silicon-copper acts first as a deoxidizer in accordance with the equation: $2Cu_2O + Si = SiO_2 + 4Cu$. When its action in this regard

[6] The proportions of hydrogen and oxygen actually present were so small that they can be left out of discussion here.

is complete, it *may* act as an agent for increasing the ability of copper to hold gases in solid solution. It cannot, however, act in this way until its affinity for oxygen has been completely satisfied.

8. The absolute necessity of ascertaining the condition of copper in respect of its content of cuprous oxide before determining the solubility of any gas in the copper is made quite evident.

Acknowledgments

The author wishes to acknowledge his indebtedness to the Westinghouse Electric & Manufacturing Co., in whose foundry and research laboratory this work was done, for permission to publish these results.

Thanks also are due to N. A. Ziegler for the analyses of the gases extracted from the test ingots and for his assistance in certain of the experiments, to R. H. Wynne for the analyses, to Dr. R. C. Reader for the analyses of the gases in the oil furnace and to Miss M. Ferguson for her assistance in the photomicrographic work.

The author is also indebted to P. H. Brace, C. R. Stevens and H. F. Seifert for their encouragement and support.

DISCUSSION

O. W. Ellis.—There is one point in regard to our analyses to which attention should be called; that is, the fact that the method of analysis employed by us was unable to detect the presence of sulfur dioxide in the gases extracted from the copper, so that when carbon dioxide is referred to in the tables it may mean carbon dioxide plus sulfur dioxide.

Another point worthy of remark is the statement on p. 467 in regard to the elimination of zinc oxide from brass. While we are certain that cuprous oxide can be reduced to metallic copper when oxide-bearing copper is melted in the oil furnace under suitable conditions, we are not sure that zinc oxide might not be similarly reduced to metallic zinc, given sufficient time. Other things being equal, however, zinc oxide and cuprous oxide differ so widely in their reducibility that the statement made in conclusion 5 can be accepted as definitive.

R. S. Dean, Chicago, Ill.—If water vapor may be present in copper, to that extent we are introducing error into our ordinary oxygen determination in copper, because presumably we weigh not only the water from the reduction of oxide but also the water present as water vapor. I do not know whether the quantity would be enough to affect the analysis in an 0.03 or 0.04 per cent. copper.

S. L. Hoyt, Schenectady, N. Y.—I have not attempted to follow this line of work at all and the answer to my question may be obvious to Professor Ellis or those who have worked in it, but I could not help wondering about the CO_2 to CO ratio. As I recall it, the CO_2 is almost completely decomposed at temperatures corresponding to the melting point of copper, and under those circumstances, I do not see how there can be as much CO_2 present in the copper as is represented by these analyses, unless possibly the CO_2 to CO ratio is affected during the cooling of those gases to room temperature, which might depend upon something present which would act as a catalyzer.

O. W. Ellis.—Dr. Dean's remarks are to the point. It should be noted, however, that the weight of water vapor found in our case never exceeded 0.0034 per cent. of the weight of the copper.

Dr. Hoyt's question was one that has puzzled us also. All that can be said at the moment is that, after considerable discussion with various members of the Westinghouse Research staff and a review of the literature, we decided to assume that in the presence of copper the carbon dioxide retained its identity even at those temperatures at which dissociation normally occurs. (See, for example, Iwasé's discussion on the solubility of CO_2 in copper.) As stated in the paper, "much remains to be done in this connection," and, on this account, we feel that the views expressed therein must be considered as likely to change in the light of fuller knowledge.

Gases in a Sample of Overpoled Fire-refined Copper

By O. W. Ellis,* East Pittsburgh, Pa.

(New York Meeting, February, 1929)

The writer has dealt with the effect of various methods of melting copper upon the gas content of the metal.[1] The copper referred to in his earlier paper was melted in the foundry both in the oil furnace and the electric furnace. As the metal did not measure up to conductivity

Fig. 1.—Ingot of overpoled copper.

standard, the term "casting copper" was applied to the material in the title of the paper.

It was thought that some information in regard to the gases in a sample of overpoled copper might also be of interest, and through the courtesy of C. R. Stevens, superintendent of the copper mill of the Westinghouse Elec. & Mfg. Co., such a sample was obtained. The metal was chill-cast in the form of an ingot about 7 in. long, 2½ in. deep (from the base to the raised surface of the ingot) and from 1⅜ to 1⅞ in. wide. A photograph of part of the ingot is shown in Fig. 1. The effect of overpoling on the surface of the metal is here quite clearly shown.

* Metallurgical Engineer, Research Dept., Westinghouse Elec. & Mfg. Co.

[1] O. W. Ellis: Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. See page 443.

In preparing this sample of overpoled copper, a charge of approximately 40,000 lb. of refined copper scrap, containing small quantities of soldered leads, connectors, etc., such as is referred to in the paper by Pilling and Halliwell[2] and is described in more detail in the discussion of that paper by Stevens, Pilling and Bassett, was, after refining, brought to pitch by poling with green hard wood. From the copper in this condition a small ladleful was taken and was well stirred with a small pole of the same wood that was used in treating the major portion of the charge. The overpoled metal thus obtained was poured into the mold described.

The analysis of the metal was as follows: copper, 99.96; silicon, 0.001; tin, 0.01; lead, 0.013; iron, 0.012; zinc, 0.01 per cent.

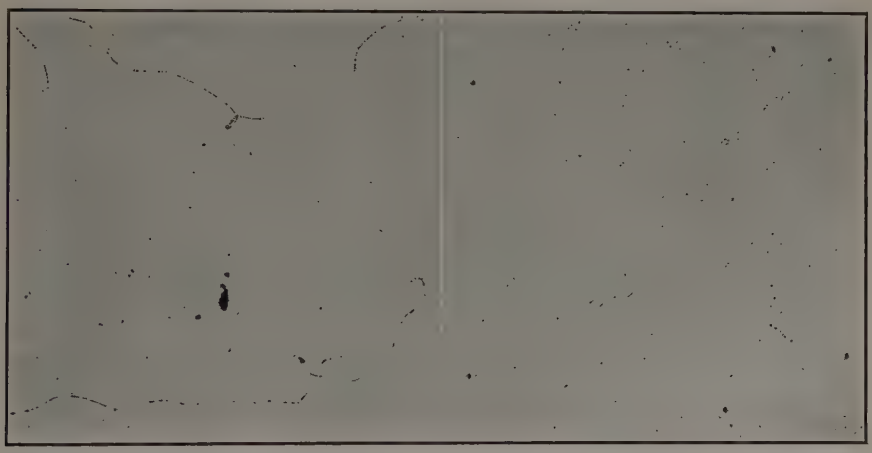


FIG. 2.—STRUCTURE OF METAL 10 MM. FROM TOP OF INGOT SHOWN IN FIG. 1. × 100.

FIG. 3.—STRUCTURE OF METAL BELOW 10-MM. LEVEL. MOST OF THE SPOTS ARE BLOWHOLES. × 100.

Microscopic examination of a cross-section of the ingot showed that some oxidation of the metal had occurred during its sojourn in the mold subsequent to pouring, a hypoeutectic structure (copper-cuprous oxide) being observed to a depth of 10 mm. from the top of the ingot. The proportion of cuprous oxide in the metal decreased very rapidly as the distance from the surface of the ingot increased. The structure of the metal at a depth of 10 mm. was as shown in Fig. 2, the line of oxide particles at the lower part of the photomicrograph forming, as it were, a boundary between the oxidized and the unoxidized portions of the ingot. The amount of oxide at lower levels in the ingot was so little as to make it hard to detect. Fig. 3 shows the structure of the metal at these lower levels. In this photomicrograph the spots in almost all cases represent not oxide, but blowholes.

[2] N. B. Pilling and G. P. Halliwell: Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper. *Trans.* (1926) **73**, 679; discussion, 692.

Analysis of the Gases

An analysis of the gases extracted from one-half of the ingot shown in Fig. 1 is given in Table 1.

Table 1.—*Analysis of Gases from One-half of Ingot*

Ingot Number	Gas	Weight of Gas in Per Cent. of		Volume of Gas in Per Cent. of	
		Copper	Total Gas	Copper	Total Gas
23	CO_2.....	0.00146	84.6	5.6	69.1
	H_2O.....	0.00026	15.4	2.5	30.9
	Carbon.....		23.1		
	Total.....			8.1	

The outstanding features of this analysis are as follows:

1. The complete absence of nitrogen from the gaseous mixture.
2. The complete absence of oxygen from the gaseous mixture.
3. The complete absence of carbon monoxide from the gaseous mixture.
4. The complete absence of hydrogen from the gaseous mixture.
5. The relatively small quantity of gas retained in the solid metal.
6. The percentage of carbon (23.1 per cent.) by weight in the gaseous mixture.

Absence of Nitrogen

The absence of nitrogen from the gaseous mixture might be explained by assuming that the rate of cooling of the ingot was insufficiently rapid to insure retention of nitrogen in the metal. It has been shown by the writer that practically all the nitrogen in copper is evolved on slow cooling of the metal through the melting point.[3] It is surprising, however, that no nitrogen has been retained in this chill casting. The question arises whether a more or less complete removal of nitrogen from the liquid metal is effected during the poling period. This question, which can not be answered here, is justified by the fact that solid copper after being melted under reducing conditions in the electric furnace retains quite an appreciable amount of nitrogen when cast in the form of small sand castings—castings which, it may be well to note, would cool only slightly, if at all, more quickly than the chill casting now under discussion.

Absence of Oxygen

The absence of oxygen is not surprising. Castings made of copper which, prior to fusion in the oil furnace, had contained cuprous oxide have been shown by the writer to be practically free from occluded oxygen, such gaseous oxygen as was contained in the molten metal being

[3] See page 466.

evolved during its cooling. As in the case of nitrogen the question arises as to whether the poling eliminates this gas, a question which the writer's tests do not answer.

Absence of Carbon Monoxide

The absence of carbon monoxide is somewhat surprising, though it may be noted that copper melted under reducing conditions in the electric furnace is free from this gas.[4] There is an essential difference in this connection which, however, must not be overlooked. The electrically fused copper referred to was to all intents and purposes free from cuprous oxide when charged into the furnace, whereas the overpoled copper was thoroughly oxidized prior to poling.

Absence of Hydrogen

The total absence of hydrogen is somewhat surprising, in view of the fact that the copper now in question was oxidized prior to poling. Oxidized copper when melted in the oil furnace was found by the writer to contain more hydrogen than oxide-free copper; one might, therefore, have expected some hydrogen in overpoled copper.

Small Amount of Gas Retained

The small amount of gas retained by the metal is not surprising in view of the fact that oxide-free copper melted under reducing conditions in the electric furnace contains less gas than either metal melted in the oil furnace or metal melted under oxidizing conditions in the electric furnace. It is impossible to compare the results of the present experiment with those referred to in the previous paper,[5] on account of the differences in cooling rate which must have existed. Nevertheless the difference in cooling rate can not have been so great as to make it impossible to infer that overpoled copper is more free from occluded gas than casting copper melted under reducing conditions in the electric furnace.

Percentage of Carbon

The fact that the percentage of carbon (23.1 per cent.) present in the form of carbon dioxide is of the same order as that found in the casting copper melted under oxidizing conditions in the writer's previous experiments[6]—*viz.*, 21.9 average—is one that seems worthy of note. Variations in water vapor content will have their effect on this quantity—*i.e.*, the percentage of carbon—but they can not account for the remarkable difference between the carbon content of the gases extracted from oxide-free copper melted in the electric furnace under reducing conditions and that of the gases extracted from copper containing oxide. The fact that this overpoled copper contains an amount of carbon which approximates closely that which was present in the oxidized copper of the writer's

[4] See page 462.
[5] See page 443.
[6] See page 457.

previous experiments raises the question whether copper, once oxidized, will not retain its content of carbon unchanged even after being brought to pitch, or overpoled. If this question can be affirmatively answered, the low-carbon content of the gases extracted from the unoxidized casting copper melted in the electric furnace in the writer's previous experiments might possibly be explained on the basis that the particular batch of copper used in this experiment had been thoroughly deoxidized before being charged into the furnace. It is of interest to observe that chemical analysis of this copper revealed an appreciable quantity (0.4 ± per cent.) of zinc in the copper. This zinc may have been the cause of the deoxidation of the metal in the first instance.

Conclusion

These speculations may or may not be of value in arriving at a logical explanation of these and other analyses of the gases extracted from copper. It is believed, however, that they merit record, in view of the fact that they may form a basis for future discussion of the subject of gases in copper.

The writer desires to express his appreciation of the cooperation of those upon whose work this contribution is largely based—R. H. Wynne, to whom is due the analysis of the copper, and N. A. Ziegler, to whom is due the analysis of the gases extracted from the ingot.

DISCUSSION

R. C. Dalzell, Cambridge, Mass.—The fact that Mr. Ellis has ignored SO_2 in analyzing the gases in copper may or may not be important. No work has been reported which justifies the assumption that this gas is not present in the evolved or occluded gases. At Baltimore we performed a rough experiment in which we found 20 parts per million of SO_2 in the gases given off by a solidifying flatcake. The apparatus used for collecting the gases was crude, but even if the SO_2 is five times as concentrated as this it constitutes only 0.01 per cent. of the gases evolved. We have not yet remelted any copper in vacuum for the purpose of testing for SO_2 in the occluded gases, but we are now carrying on experiments of this nature in the Metallurgical Laboratory of Harvard University.

O. W. Ellis.—Mr. Dalzell's remarks regarding sulfur dioxide are of considerable importance. The possibility of the presence of this gas has, however, not been overlooked by the author, who has fully recognized that any sulfur dioxide would, by the method which was adopted by Mr. Ziegler in carrying out these gas analyses, be measured with the carbon dioxide. This is clearly a defect in the physical method of measuring the proportion of gases present in a gaseous mixture such as is discussed in this and the author's previous paper.

While it cannot be denied that sulfur dioxide may be present in copper, in fact that it is likely to be present, it is interesting to note the uniformity of carbon content in the gases extracted from the samples which have been examined by the author. This uniformity of carbon content tends to confirm, but does not by any means prove, the view that the proportion of sulfur dioxide in the gases examined must have been relatively small.

Incipient Shrinkage in Some Non-ferrous Alloys

By J. W. Bolton* and S. A. Weigand,† Cincinnati, Ohio

(New York Meeting, February, 1929)

Production of sound bronze castings is a matter of great practical interest to users and manufacturers of high-grade non-ferrous engineering specialties. Although there has been much excellent research in this field, there still remains some confusion regarding the fundamental principles underlying production of really sound bronze. The literature of the past 20 years on this subject indicates that the prevailing opinion of metallurgists and foundrymen has been that unsoundness in bronze is due generally to oxidation. The following references are typical.

Review of Literature

Carpenter and Edwards[1] state that when gun metal is melted the alloy dissolves gas, the amount increasing with rise in temperature and duration of the melting. The solubility of the gas diminishes during the fall in temperature and it escapes through the liquid metal. At the moment of incipient solidification there is an evolution of gas.

Sperry[2] says that by using charcoal a reducing atmosphere is supplied whereby oxidation is prevented, and this also prevents gases from coming in contact with the metal.

Logan[3] says that many of the troubles that occur in non-ferrous castings are the direct result of one thing—oxidized material. He mentions how readily copper absorbs oxygen when molten, but does not mention the harmful effects of reducing conditions as observed in overpoled copper.

Guillemin and Delachanal[4] investigated the gases occluded in bronze and found that the better bronzes contained mostly hydrogen while the poorer ones had a larger proportion of carbon monoxide and carbon dioxide.

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* Chief Metallurgist, The Lunkenheimer Co.

† Research Metallurgist, The Lunkenheimer Co.

[1] H. C. H. Carpenter and C. A. Edwards: Production of Non-ferrous Castings to Withstand High Pressure. *Castings* (1911) **7,** 121.

[2] E. S. Sperry: Fluxes as Applied to the Brass Foundry. *Brass World* (1910) **6,** 239.

[3] Logan: Non-ferrous Foundry Practice. Inst. of British Foundrymen.

[4] G. Guillemin and B. Delachanal. Recherche sur les gaz occlus contenus dans les alliages de cuivre. *Compt. rend.* (1910) **151,** 881.

Primrose[5] says that gun metal should not be held molten for a long time as it absorbs gases and then forms blowholes.

Clarke[6] believes that high pouring temperatures are critical chiefly because of extreme "oxidation" and the occlusion and expulsion of gases resulting in porosity.

Wolf and Burr[7] made analyses of atmospheres of furnaces using natural gas and found that with a slight excess of carbon monoxide (not over 1.0 per cent.) no oxidation of the metal occurred and high-quality castings were produced.

Dewrance[8] points out that no benefits were derived from the deoxidation or oxidation of the metal. He does not mention the benefits derived from preventing absorption of reducing gases by the molten metal.

Rawdon[9] says that in addition to oxide films found in 88-10-2 bronze, most of the test specimens examined show some porosity. He concludes that the presence of oxides far outranks any other cause of weakness.

Frohman[10] advocates the use of a layer of charcoal or coke on top of the metal to insure a reducing atmosphere.

Flinn and Jonson[11] say that the most common defect results from the inclusion of oxide in the metal.

Carpenter and Elam[12] in 1918 could find no information about the gases in the fluid alloy. They were unable to find any analyses of these gases, or any record of attempts to rid the fluid alloy of them. Carpenter apparently does not place the blame on oxygen for unsoundness in bronze. In the analysis of the gases from sections of sound and unsound bronze castings, he found the greatest variation in amount in carbon monoxide, but said that there was nothing to indicate that it has any relation to unsoundness.

Comstock[13] found that the oxide films so frequent in commercial bronzes may be caused by either the volatile oxides of zinc or phosphorus or by dissolved gases thrown out of solution when the metal solidifies. The data showed that the oxides of tin, alumina, etc., are not similar in

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[5] H. S. Primrose: Modern Practice of Brass Founding. *Castings* (1912) **10,** 174.

[6] R. R. Clarke: Pouring Temperatures as Affecting Casting Shrinkage and Solidity. *Trans.* Amer. Foundrymen's Assn. (1921) **29,** 533.

[7] F. L. Wolf and R. B. Burr: Tests of Natural Gas Fired, Brass Melting Furnaces under Factory Operating Conditions. *Trans.* Amer. Inst. Metals (1915) **9,** 343.

[8] J. Dewrance: Bronze. *Jnl.* Inst. Metals (1914) **11,** 214.

[9] H. S. Rawdon: Standard Test Specimen of Zinc-bronze. *Trans.* Amer. Inst. Metals (1915) **9,** 60.

[10] Frohman: Note on the Question of Fluxes. *Jnl.* Inst. Metals (1917) **18,** 415.

[11] A. D. Flinn and E. Jonson: Inspection of Brass and Bronze. *Proc.* Amer. Soc. Test. Mat. (1917) **17,** Pt. 2, 213.

[12] H. C. H. Carpenter and C. F. Elam: An Investigation on Unsound Castings of Admiralty Bronze. *Jnl.* Inst. Metals (1918) **19,** 155.

[13] G. F. Comstock: Non-metallic Inclusions in Bronze and Brass. *Trans.* (1919) **60,** 386.

appearance to the intercrystalline films or cavities to which porosity is due. The formation of the latter was not explained.

Bamford and Ballard[14] concluded that it is impossible seriously to impair the mechanical properties of the metal by overheating.[15]

Anderson and Capps[16] say that carbon monoxide is a frequent constituent of melting-furnace atmospheres; also, that under normal conditions the atmosphere of most electric furnaces contains a high percentage of carbon monoxide. In the open-flame furnace of the Schwartz type, they found a maximum of 11.0 per cent. of carbon monoxide during the melting of aluminum. In numerous cases it was absent during the melting. On 38 samples it averaged 2.9 per cent. In the Detroit electric furnace, melting No. 12 aluminum alloy, they found a maximum of 42.8 per cent. carbon monoxide, a minimum of 1.5 per cent., and on 15 samples, an average of 20.7 per cent. They make no comments regarding the effects of the various gases on the metal.

Keizo Iwasé[17] declares that carbon monoxide and carbon dioxide are soluble in liquid copper, the solubility decreasing with rising temperature (see Fig. 13).

Edwards[18] says that unsoundness is caused by hydrogen, oxygen, and sulfur in the liquid metal, these separating out as the metal solidifies.

Woyski and Boeck[19] say, "Gas and shrinkage cause porous metal and intercrystalline fissures." They also say, "Oxidation, gassing and shrinkage may produce effects very similar." While the modern trend is toward this viewpoint, one still finds many references to "oxidation" as the most common cause of porosity.

Literature of copper metallurgy contains many data on the influence of various gases upon copper. While highly suggestive, any apparent analogies between behavior of copper and of bronzes should be examined with caution. A recent paper of value is that by O. W. Ellis,[20] who directs attention to the work of Iwasé, showing marked change in absorption coefficients for various gases above and below the liquidus.

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[14] T. G. Bamford and W. E. Ballard: Influence of Gases on High-grade Brass. *Jnl.* Inst. Metals (1920) **24,** 155.

[15] This is possibly true, provided the atmosphere is kept as neutral as possible.

[16] R. J. Anderson and J. H. Capps: Constitution of Gas Atmospheres in Aluminum-alloy Melting Furnaces. *Chem. & Met. Eng.* (1921) **25,** 54.

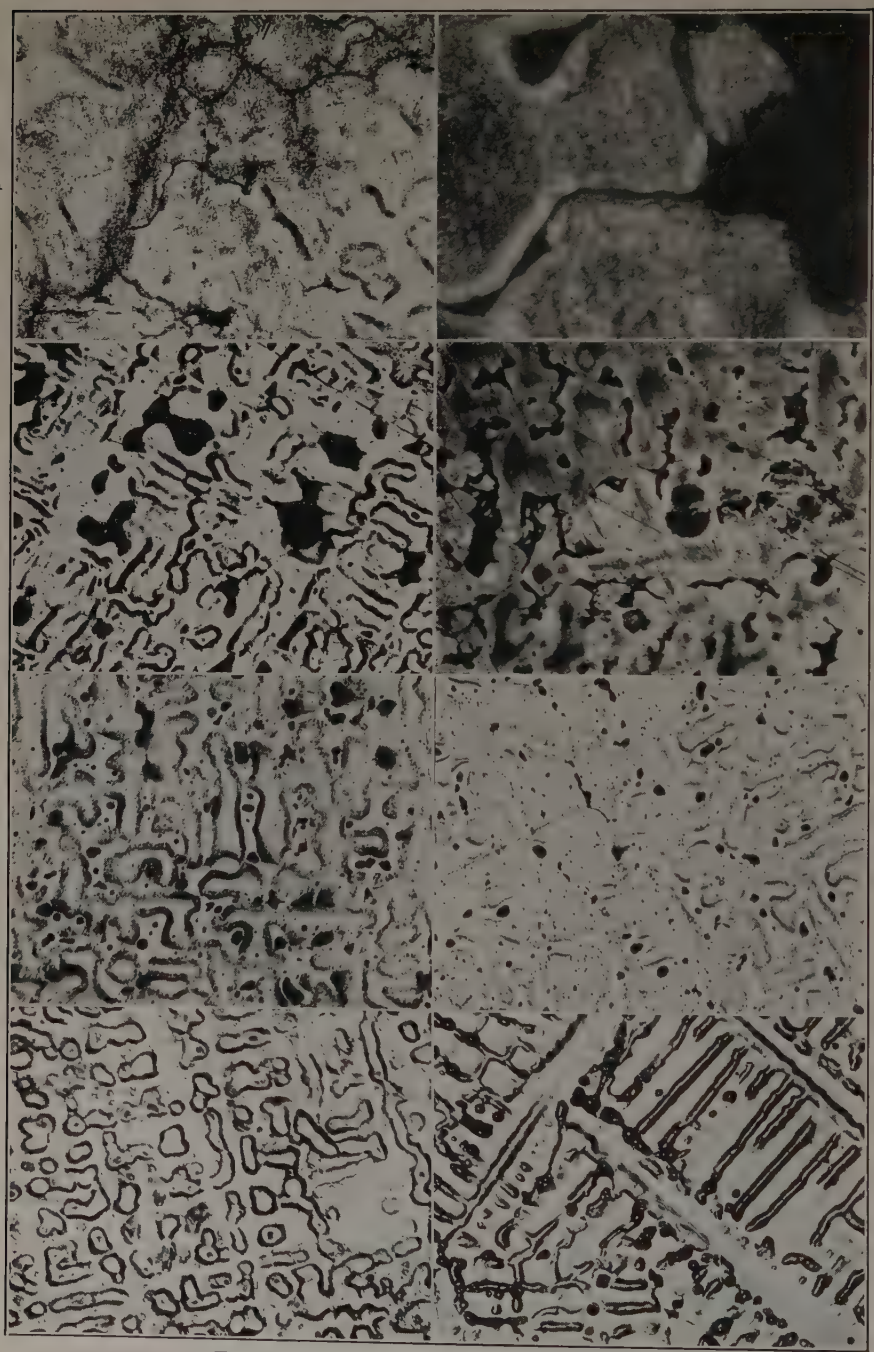
Gases in Aluminum Furnaces and Their Analysis. *Idem* (1921) **24,** 1019.

[17] K. Iwasé: Occlusion of Gases by Metals and Alloys in Liquid and Solid States. *Sci. Repts.* Tohoku Imp. Univ. [1] (1926) **15,** 531.

[18] C. A. Edwards: Some Problems of Casting Metals and Alloys. *Bull.* British Non-ferrous Metals Research Assn. (1926) **17,** 11.

[19] B. Woyski and J. W. Boeck: Gas Absorption and Oxidation of Non-ferrous Metals. *Trans.* (1923) **68,** 861.

[20] O. W. Ellis: Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. See page 443.



FIGS. 1–8.—CAPTIONS ON OPPOSITE PAGE

Ellis indicates that copper castings made under reducing conditions contain neither hydrogen nor carbon monoxide. He also calls attention to the necessity for ascertaining the condition of copper in respect to its content of cuprous oxide before determining the gas solubility.

Examining tin-antimony-copper-lead alloys, Cowan[21] finds minute shrinkage cavities due to change in volume between solid and liquid phases of a low freezing point component where it last freezes after the bulk of the alloy has solidified at higher temperature.

Porosity in Bronze Castings

Unsoundness, or porosity, in bronze castings may arise from a number of causes; for example, cracks, blowholes, sand inclusions, dross, and cold shuts may cause leakage. However, the most serious cause of porosity is intercrystalline fissures, as shown in Figs. 1 to 6. When castings show this intercrystalline porosity, resulting in seepage under pressure, the fracture often has a reddish to chocolate appearance. This condition is commonly termed "oxidation."

The seriousness of bronze porosity varies with the design and service of the product. For example, the internal soundness of ornamental castings is a matter of little moment. It appears that many bearing metals are not seriously affected by slight porosity. Plumbers' goods, some fittings, and similar castings that have little machine work upon them, need not be as internally sound as highly finished articles such as valves, gears, etc.

The character of product of The Lunkenheimer Co. (valves and engineering specialties) demands severe inspection standards, and consequently use of very dense, sound metal (see Figs. 7 and 8). Discussion in this paper is devoted to intercrystalline porosity, often termed oxidation. The alloy most intensively studied is a high-grade steam bronze containing 6 per cent. tin, 4 per cent. zinc, under 2 per cent. lead, and 0.5 per cent. nickel.

For the greater period of this investigation all new metals were virgin. C. R. copper was used throughout.

[21] W. A. Cowan: *Jnl.* Inst. Metals (1928) **39.** This author refers to work by Guillet, Galibourg and Ballay: Les Retassures Intercrystallines. *Rev. de Mét.* (1925) and Porosity and Physical Properties of Tombac. Abst. in *Cont. Met. & Chem. Eng.* (1927) **2,** 213.

Fig. 1.—Navy G metal from pump. × 100.
Fig. 2.—Same as Fig. 1. × 500.
Fig. 3.—Gas passed through metal when molten in crucible. × 100.
Fig. 4.—Badly gassed high-tin bronze.
Fig. 5.—Unsound bronze poured at 2120° F. Tensile strength, 37,558 lb. per sq. in. × 100.
Fig. 6.—Same as Fig. 5, but poured at 1920° F. × 100.
Fig. 7.—Sound bronze. Neutral atmosphere. × 100.
Fig. 8.—Sound monel metal. × 100.

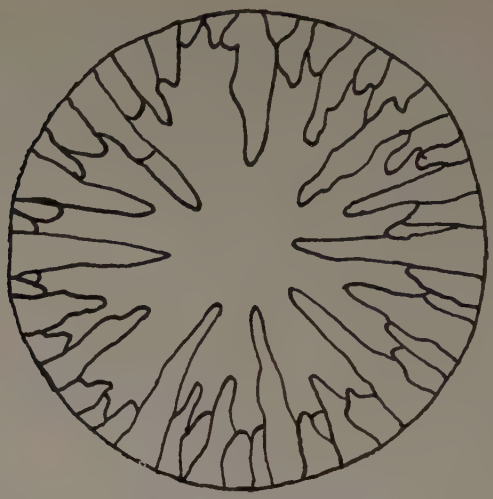
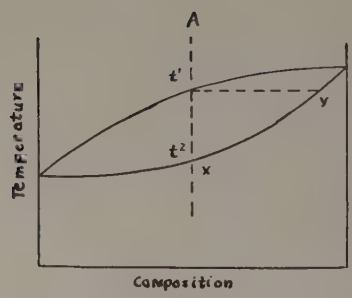


FIG. 9.—PRIMARY COLUMNAR CRYSTALLIZATION.
This formation is most evident when the metal is poured at rather high temperature

(A)



(B)

FIG. 10.—CORING. A, EFFECT; B, CONSTITUTION DIAGRAM.
During solidification of alloys of the solid-solution type, selective crystallization causes the first particles to be different in chemical composition from those separating later. The reasons for this are made clear by the constitution diagram. Each layer is different in composition from the preceding one, the number of layers is very great.

Our investigations show that a furnace atmosphere high in carbon monoxide has a most deleterious effect on the soundness of castings. Good design, proper pouring temperatures and proper gating are conducive to good castings, but while wrong pouring temperatures affect the density and thereby the strength of the metal, it is difficult to get internally sound castings from metal melted in gas, oil or electric furnace with an atmosphere charged with an excess of carbon monoxide.

Alloys of the type herein considered are mostly solid solutions, with a large temperature interval between solidus and liquidus. This temperature interval, at certain pouring temperatures, promotes primary columnar crystallization (Fig. 9). The alloys also are subject to coring (Fig. 10), since time for equilibrium is not available in castings practice. Furthermore, such alloys are more influenced by liquid shrinkage than is supposed. Naturally, alloys with the characteristics enumerated are subject to segregation.

In the preliminary steps in the investigation, it was evident that castings porous on the hydrostatic test always exhibited a discolored fracture. (Pressure used is at least 3½ times the recommended working pressure.) It was thought that this fracture appearance would afford an easy checkup of lots made under special conditions in the foundry. Some lots were run, foundry practice looked good, but at the test it was evident that no improvement had resulted. A clear or uncolored fracture in the foundry does not necessarily mean a sound casting, although the experienced eye can make a clever guess due to certain characteristics in the fracture.

In certain cases other than the valve industry, the writers have seen discolored fractures in the foundry and in test bars. When the foundry fracture is discolored the porosity is very bad. In many cases where porosity is not excessive, the only answer short of the hydrostatic or pneumatic test is the microscope. The latter is a very severe judge, as metal sound enough for most practical purposes may still have some interstices evident on magnification.

Evidences of Incipient Shrinkage

After extended study of operating conditions, castings design, microstructure of alloys, etc., it was concluded that the fundamental causes of intercrystalline porosity are related to the shrinkage characteristics of the alloy; that, in fact, such porosity may be aptly termed "incipient shrinkage." The following evidences were considered:

1. An ordinary foundry shrinkage cavity is characterized by varying amounts of perfect dendritic crystal skeletons. Just around the cavity is a spongy area. This may not be visible to the naked eye on either a machined or fractured surface but is quite evident after deep etching. Further away from the shrinkage cavity are areas that appear visually

sound even on deep etching. If these visually sound areas are etched and examined under the microscope a porous structure may be found. As the distance from the cavity is increased, the metal becomes more sound.

2. Porosity is most common in sections of improper design—for example, where heavy sections run into light. The long temperature interval between primary and final crystallization, the apparently high viscosity of these liquids, and the differences in cooling rates between light and heavy sections, all promote feeding of the light section at the expense of the adjacent heavy section and consequently cause foundry shrinkage. When tested, such shrinkages often exhibit the regular darkened fracture called oxidation.

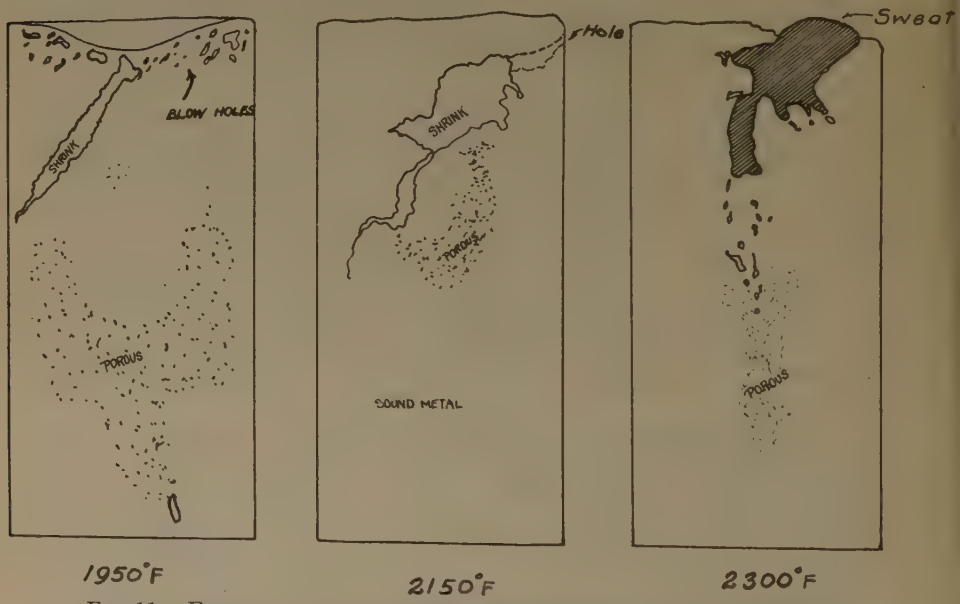


FIG. 11.—EFFECT OF POURING TEMPERATURE, SHOWING CAULIFLOWER HEAD.
Top poured; not open to air; green sand. Alloy, tin, 6 per cent.; lead, 2 per cent.; zinc, 4 per cent.; copper, 88 per cent. Bars 4-in. dia.; 10 in. long.

3. The most porous sections occur in the center of the section rather than near the skin, thus the factors influencing porosity come into play near the latter end of the solidification period. This is characteristic of ordinary foundry shrinkage. (It might be explained here that this is a reason that highly machined castings are more difficult to make sound than are castings with the skin on.)

4. Chilled castings rarely shrink or show porosity. The rapid cooling cuts down the time interval, thus minimizing temperature gradients. There is less time for selective solidification and segregation; also for the freeing of dissolved gases.

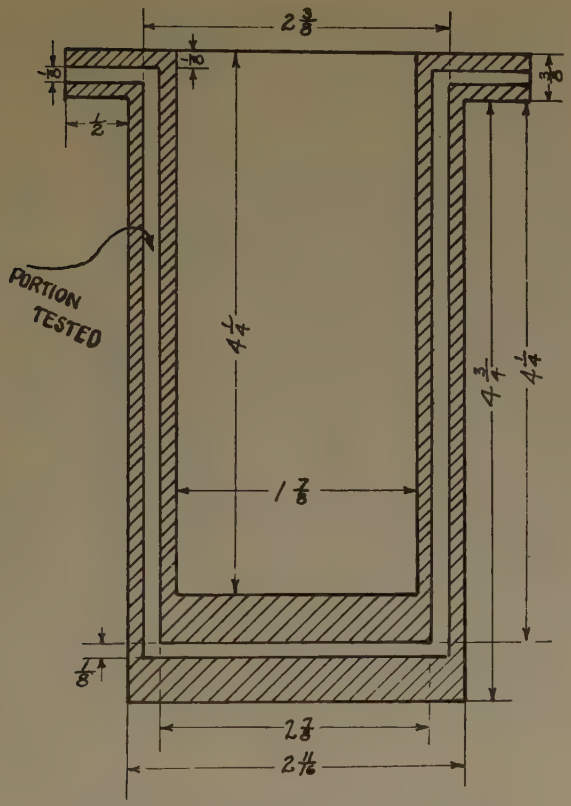


FIG. 12.—PERMEABILITY CASTING. "HI-HAT."
Cross-hatched area represents metal machined away.

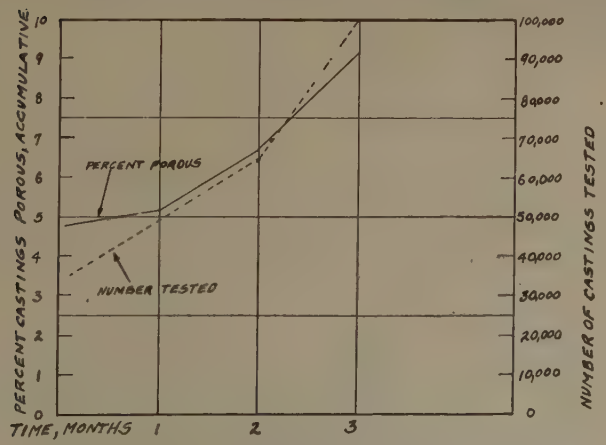


FIG. 13.—EFFECT OF REDUCING FLAME IN GAS FURNACE.

Only castings machined all over were tabulated, and of those only 25 chronic offenders. When the reducing flame was discontinued the porosity dropped back, and when further changes were made the trouble on these castings was under 1.5 per cent.

5. It is well known that proper pouring temperatures help to minimize porosity. It is easy to show that castings poured at too low a temperature cannot "feed" properly, and as a result often are unsound (a shrinkage effect). Furthermore, when poured at too high a temperature there is actual ejection of metal (causing cauliflower head) with consequent unsoundness beneath (see Fig. 11). This is probably due to gas rejection as well as to external contraction. The effects of pouring temperature on strength are quite marked when metal is melted under reducing atmospheres. As in other metals, the pouring temperature affects the crystallization characteristics.

6. Proper gating helps to minimize porosity. The only way it can do this is by helping to counteract the tendency toward foundry shrinkage. Porous castings, which show the characteristic darkened fracture termed oxidation, often can be made reasonably sound by proper gating.

7. Dissolved gases play a part in causing porosity. At first glance their effect may not seem related to shrinkage. During crystallization the mother liquor becomes more and more saturated with gases. At the moment of solidification their solubility is greatly diminished (see Fig. 1 on page 444). Suppose that the saturation is excessive for solid metal, and that gases are rejected in the crystal interstices. This prevents feed back of the metal—causes shrinkage by preventing feed through back pressure rather than by pulling away metal, as a thin metal section would. In either case the effect is the same—insufficiency of liquid metal, hence shrinkage. Or take another illustration, when the metal is just saturated with gases, contraction (pull) sets in in the plastic material. Pressure is lowered—there is a force for evacuation—then some of the gas is freed more readily. This allows the contraction to pull apart the plastic crystals all the more easily.

Investigation of Incipient Shrinkage

Armed with the hypothesis that all intercrystalline porosity is incipient shrinkage, hence amenable to the same remedies as ordinary foundry shrinkage, practical work was undertaken on a large scale. Three lines of attack were outlined; namely, gating, furnace atmosphere, pouring temperature. Careful attention also was given to presence of impurities, to effect of fluxes and reactions of the furnace lining.

In order to have a prompt checkup, the permeability test cup (Fig. 15) was utilized. Careful check was kept on strength of metal, and detailed records of operating conditions were kept on many castings that were chronic offenders. As always, a record of general porosity was kept up. On the electric furnace a complete operating log was kept.

Two types of furnace were used in the foundries, the open gas furnace and the indirect-arc electric furnace of 750-lb. capacity.

Study of the Gas Furnace

The gas furnace was studied first. The fuel used was mixed natural and artificial gas of the following average composition: ethane, 13.55 per cent.; methane, 57.60; carbon monoxide, 11.53; hydrogen, 12.73; nitrogen, 2.69 (by diff.); carbon dioxide, 1.90; oxygen, trace.

In spite of the fact that regular operating methods melted the metal free from excessive dross, it was feared that improper mixing of the gases in the burners allowed oxidation, therefore some 100,000 castings were made, over a period of several months, with the furnace atmosphere of the following average composition: carbon dioxide, 3.96 per cent.; oxygen, 1.20; carbon monoxide, 6.78.

This gives what the foundrymen term a "long" flame and resulted in a rapid increase in porosity, as shown in Fig. 13. It was very evident that while the old practice was not ideal, increase in carbon monoxide and other reducing gases made things bad. It was very obvious that the burners and arrangement of air and gas were improper. Better mixing burners were substituted with the following average result: carbon dioxide, 11.8 per cent.; oxygen, 0.4; carbon monoxide, 0.9. More nearly neutral atmospheres effected radical increase in soundness in castings from these furnaces.

Study of Indirect-arc Furnace

Meanwhile records of the indirect-arc furnace were being analyzed. Shortly after installation of this furnace porosity began to mount (see Fig. 14). As the furnace is of 750-lb. capacity, the number of small castings poured from it is very large. Examination of the furnace atmosphere showed:

	Maximum, Per Cent.	Minimum, Per Cent.	Average, Per Cent.
Carbon dioxide	16.5	4.8	10.0
Carbon monoxide	68.6	1.1	25.0
Oxygen	trace	trace	trace

The ladles (dried and preheated) often boiled violently. This was particularly noticeable when charcoal was placed on the bottom—an action which from later experience we believe is analogous to the action of sand thrown into air-charged water. It was deemed desirable to produce a more neutral atmosphere in this furnace before working on gating and pouring temperatures. First of all, the bricks were left out

of the spout. This made little change in atmospheric composition. Then other means were taken to produce a neutral atmosphere. Gas analyses are taken twice daily. The following average monthly analysis

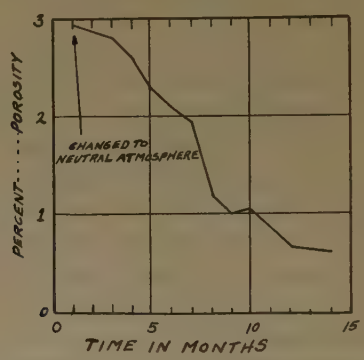


FIG. 14.—IMPROVEMENT WITH NEUTRAL ATMOSPHERE.

Most of the castings involved in these tests were melted in the indirect-arc furnace. Before installation of this furnace, porosity ran about 1.5 per cent.

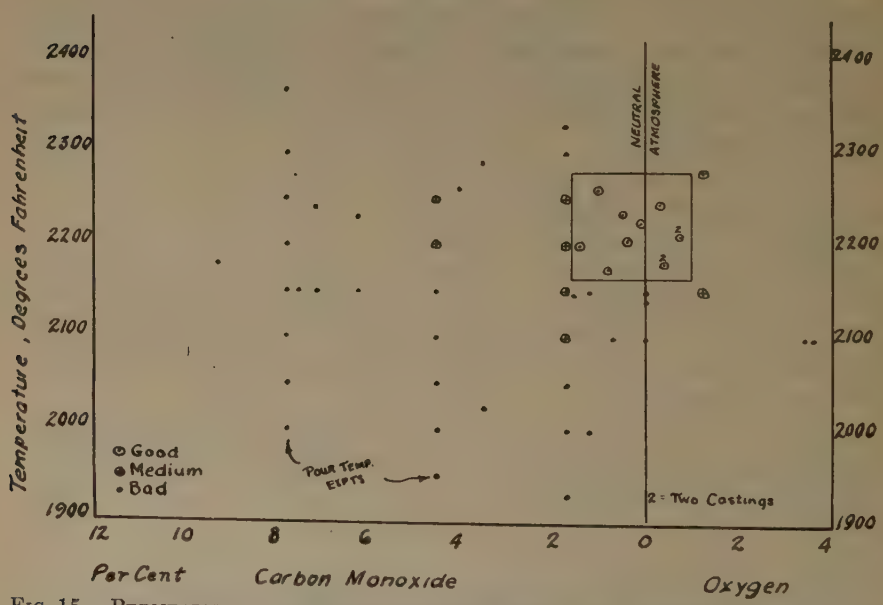


FIG. 15.—PERMEABILITY CASTING CHART SHOWS DESIRABILITY OF NEUTRAL ATMOSPHERE.

is typical of present practice: carbon dioxide, 16.9 per cent.; carbon monoxide, 0.6; oxygen, 0.5. (See Fig. 15.)

It was thought at one time that some of the troubles might be due to impurities added inadvertently with the charge or picked up from the

furnace lining. Phosphor copper is added to counteract possible oxides, the amount varying from enough to produce a trace to enough to give 0.02 per cent. in the finished product. Experiments showed that greater amounts discolored the castings, but gave no apparent improvement. Sulfur is present in small amounts, usually well under 0.02 per cent. With composition ingot metal 50 per cent. of new metal charge, this is somewhat increased, but it is always kept well under 0.04 per cent. When barium sulfate was used in experimental lots to offset the alleged evil effect of possible silicon contamination, the sulfur very rapidly mounted to 0.085 per cent., but no improvement was noted. Recent analyses of carbon in this metal by steel-combustion methods show 0.010 to 0.016 per cent. carbon (by weight). This method appears open to question.

Antimony is present in slight traces only. Analyses using the ammonium salt of aurin tricarboxylic acid indicate the virtual absence of aluminum. No analyses were made for arsenic or silver. Iron is low.

Effect of Silicon

At one time we were earnestly advised that silicon from the furnace lining was the alpha and omega of many bronze-foundry troubles. This theory was given a thorough trial: Analytical methods were checked, sound and unsound castings were examined, and tests were made on metal deliberately contaminated with silicon.

Check on Analytical Method

A sample of bronze, presumably silicon-free, was carefully analyzed. It showed very slight traces of silicon. (Blanks were run on acids, glassware, filter papers, etc., involved in process.) Then, to this practically silicon-free bronze a definite amount of analyzed silicon bronze was added. (We happen to make this metal regularly.) We weighed out a certain amount of silicon-free bronze in a beaker and added a definite weight of silicon bronze. (We did not melt the two, as the percentage of silicon then would be problematical.) The amount of silicon added in this manner was 0.012 per cent. Analysis showed 0.014 per cent. recovered—an additive error of one part in 50,000 (10-gram samples).

Examination of Castings

We took several lots of regular castings, made under neutral conditions and testing 100 per cent. sound, and ran a number of samples for silicon. The maximum percentage was 0.006 silicon. We then examined several castings from very spongy lots, and found only traces of silicon.

Tests on Contaminated Metals

We made up several batches to which we added 0.110 per cent. silicon and used a neutral atmosphere. Average analysis after casting was 0.030 per cent. silicon. Castings were O. K., fracture good, and average tensile was 39,459 lb. per square inch.

In our work the danger of contamination with silicon from monel metal, silicon bronze, etc., is present at all times. With the diligence and constant check exercised, we have yet to find as much as 0.020 per cent. in regular product, and we feel that this amount is not even remotely dangerous in low-lead bronze.

Effect of Furnace Lining

From time to time manufacturers of electric furnaces have insisted that the lining of the furnace is important in its relationship to soundness of metal melted therein. At various times we have used several types of lining material, as advised by the manufacturers, including materials containing silicate and those containing silicide. Careful study convinces us that furnace lining is not important in its relationship to quality of metal melted therein under our own operating conditions.

Basis of Operating Program

Under date of Nov. 15, 1927, we reported to The Lunkenheimer Co. management as follows: ". . . we believe that experimental work has reached a stage where diagnosis of troubles is accurate and fairly complete."

The operating program then laid out has been followed with no material modification, with most gratifying practical result. This covers melts of some 6,000,000 lb. of finished castings.

The decrease in porosity loss is shown in Fig. 14. The present loss is lower than in days of crucible melting. The average strength of the metal increased some 5000 lb. per sq. in.—from about 34,500 to nearly 40,000 lb. per sq. in.[22] Ductility was improved, and uniformity of physical properties is good. We have had up to 45,000 tensile and 61 per cent. elongation with this alloy. A. S. T. M. specifications for similar mixture call for 32,000 tensile.

Experiments with the porosity test cup are shown in Fig. 15. Gating was constant while temperature and atmospheric conditions were varied. This is a very remarkable confirmation of the soundness of the experimental method.

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[22] In December, 1927, this had increased to 41,770 lb. per sq. in. average; 44,950 maximum.

Shortly after reaching a more neutral atmosphere many castings showed large shrinkage cavities in the gates and elsewhere. This was an encouraging sign. General incipient shrinkage had been concentrated into a local shrink or drawhole, which was readily remedied by regating.

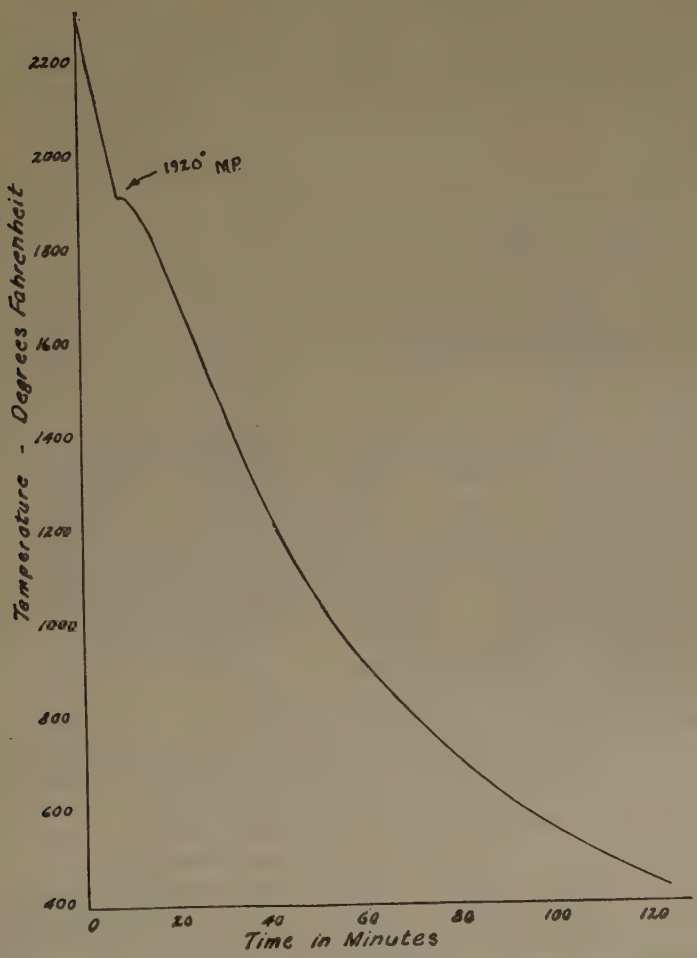

FIG. 16.—COOLING CURVE FROM CENTER OF 3-IN. DIA. TEST BLOCK, B2 BRONZE.

The Lunkenheimer metallurgical department maintains an experimental foundry where non-ferrous alloys are melted in a crucible furnace. Careful experiments, using an open-top crucible, demonstrated the deleterious effects of reducing atmospheres. In certain experiments gas was bubbled through the molten metal, which resulted in very bad

metal and a highly discolored fracture. Even in crucible melting we get the best strength and soundness when a sharp flame is used.

Conclusions

Thus it is seen that the hypothesis that internal intercrystalline porosity in bronze is due to incipient shrinkage furnishes a sound working theory for shop application. That the phenomenon is shrinkage, as termed by the foundrymen, or lack of intercrystalline coherence is quite evident and in line with metallurgical theory. That incipient shrinkage is aggravated or even caused by melting the metals under reducing atmosphere is a fact. For practical purposes the exact mechanism of this is immaterial. We regret that pressure of other work did not allow us time to include gas analysis of the metal by vacuum fusion. Just what such analyses would show is debatable. The interest lies in the occluded gases, those in the cavities. Because of the continuity of the fissures, accurate sampling presents a knotty problem. Furthermore, the relative amounts of gas in fissures and dissolved in the metal would be most difficult to establish. Carbon monoxide furnace atmosphere causes the trouble. Whether it does this by direct absorption and rejection, or through secondary reactions, is a question. Absorption and rejection is the most simple explanation. On the other hand, reaction of carbon monoxide and oxygen within the metal could result in formation of carbon dioxide. If this is the case, why does thoroughly reduced and deoxidized metal show the same phenomena on the remelt? We tried 100 per cent. remelt several times. Or the gas absorption might materially change the fluidity and feeding characteristics of the metal. If this is the case, why did we not find some changes in percentage of cold shuts on small thin castings?

We have extended the work herein indicated to include other metals, such as 85-5-5-5 bronze, 88-10-2 bronze, monel metal, nickel bronze, etc.[23] These subsequent experiences confirm our other work.

The term "oxidized metal," as used to designate all discolored fractures and porous metal, obviously is inaccurate. While it is true that such conditions can be brought about under oxidizing conditions, the natural desire of the foundryman to keep the metal loss low and avoid excessive slag will encourage him to maintain a more neutral or even reducing furnace atmosphere.

Summary

Internal porosity, commonly called oxidation, usually is traceable to general incipient shrinkage, which is very pronounced in metals

[23] In alloys containing eutectic component the theory advanced by Cowan (p. 479) merits careful consideration.

melted under reducing atmospheres. It may be minimized by running a neutral atmosphere (by gas analysis, not by eye), by proper gating, and reasonable pouring temperatures.

Acknowledgments

The writers thank the management of The Lunkenheimer Co., through whose courtesy it is possible to publish this paper. Valuable cooperation was received from George A. Seyler, Horace M. Clay, Eugene L. Bunting, and William J. Love, Jr.

DISCUSSION

H. M. St. John, Detroit, Mich.—This paper is of a pioneering nature. There has been a great deal of discussion among foundrymen and metallurgists on the various factors that enter into the unsoundness of metal, but in few instances has there been a real effort to apply modern metallurgical tools to an investigation of this problem. These tools have been developed for the study of iron and steel more particularly, but application of them to brass and bronze should reap a rich harvest; this paper is certainly an excellent first step.

W. F. Graham, Mansfield, Ohio.—This paper is more or less loaded with dynamite. It hits directly at the condition of the metal as affected by various factors that in foundry practice are not thoroughly understood today. I have read the paper a number of times, with a background of work for about 1½ years on this particular phase of brass-foundry metallurgy.

In introducing the results of their observations of the effects of incipient shrinkage, the authors have set forth in a striking way the conflict of opinion regarding the factors involved in the production of sound brass castings. In a measure their presentation has added to it.This statement is not made as a criticism of the accuracy of their data or of the sincerity of their interpretation, but in the belief that the results coming from a certain set of shop conditions cannot be set up as a measure or a guide in a study of this interesting subject by others operating under a different set of circumstances. In order to apply such results properly, one must have exact knowledge of the character of the materials melted as regards their impurities, gas content, and so forth, and the detailed effects of the melting cycle. Unfortunately the means available to evaluate these factors are most limited at the present time. Ordinary chemical analysis is only a step in this direction.

It is interesting to note that the authors feel that the eliminating of "over reduction," a term which is used as general classification of a number of effects, has made such a marked change in conditions surrounding soundness of the metal in the castings. At the Ohio Brass Co. this is a condition often reproduced in an experimental way by our research metallurgists, but not emphasized by the metallurgists studying the condition of the metal in castings, and here again we have the conflict of opinion.

It is rather unfortunate that the authors have not seen fit to detail "the other means" referred to on page 486, which brought about the operating program noted two pages farther on, as it leaves the methods of accomplishment more or less in the dark to those not familiar with the operation of this type of furnace.

The unrestricted use of the term "porosity" may be confusing to those who associate it with definite microscopic inclusion of slag, drosses, sand or oxides.

L. W. Spring, Chicago, Ill.—People who work with both steel and brass perhaps are too likely to carry thoughts from one over to the other and think that the metals behave similarly. Probably they do have many points in common. Often the practical foundryman is much afraid of overoxidation, and undoubtedly we get it many times. On the other hand, there seems to be such a thing as overdeoxidation. When one tries to do a good job in reduction in steel, he may get into just as much trouble as though he had taken out the heat before the extreme in deoxidation was reached. That may not be "incipient shrinkage." It probably is more along the line of "blowy" metal, but it is hard sometimes to tell the difference between shrinkage and some blowholes, or overdeoxidized metal.

The brass refiner is worried at times about overpoled metal, when brass is refined in the reverberatory furnace. They oxidize first to get rid of some of the things they do not want, and then deoxidize by poling with a sapling to reduce the metal, but the brass refiners seem to recognize that overpoled metal is a serious thing, and, of course, their problem, like Mr. Bolton's appears to be to stop at the right place.

It may be that it is much the same as with steel. When we try to melt down and save silicon—in other words, melt down at the right composition—we have silicon present. In superheating, gas probably is absorbed which later is given out during cooling. Mr. Bolton's problem may be a different thing, but there may be a similarity.

The author does not make it quite clear about the higher compositions. He speaks of 85, 5, 5 and 5, which, of course, means 5 per cent. lead, and he speaks of the effect of silicon. At one time we had a furnace where white hot coke in presence of an electric arc came into contact with some of the brass of approximately the composition 85, 5, 5 and 5. We got approximately the same sort of castings as when aluminum was used. Even very small quantities of aluminum brass with high lead content give castings which leak. With the metal referred to, which had no aluminum in it, we got castings which had white deposits on the outside, and gave a very high percentage of leakers. Upon analysis, we found silicon. We repeated the test by introducing into new brass certain amounts of silicon, with the same result. With approximately 5 per cent. of lead, the maximum silicon we could use without getting leakers was approximately 0.04 per cent., and judging from Mr. Bolton's statement that 0.10 per cent. was not harmful, he must have had low lead.

This brings up one more point—the right of chemist, metallurgist or foundryman to reject composition metal which he is buying. In buying composition ingots, we analyze every carload, and make a sample lot of castings from it. Occasionally, we have not found by chemical analysis reason why certain ingots will not give good castings. That is an unfortunate situation for one wants to reject the metal and the refiner, very naturally, wants to have a definite reason why. This means, of course, that the scientific man must go farther in investigating the effects of various combinations and find out the reasons why such brass will not make satisfactory castings.

J. W. Boeck, Buffalo, N. Y.—It is gratifying to me to have the results published by Mr. Woyski and myself in 1922 substantiated so aptly as they have been by Mr. Bolton and his coworker; consequently there is no adverse criticism on my part.

There is only one thing that I would like to advance as a further proof that reducing gases are detrimental and cause intercrystalline fissures, or incipient shrinkage; when the metal is melted in open-flame furnaces and badly gassed, you can actually see the gas take fire while solidification is occurring. We have observed this a number of times in experimental work.

G. E. Dalbey, East Berlin, Conn.—In the British Institute of Metals there is a paper presented by D. R. Tolst, covering the removal of gas from aluminum alloys, in which he mentions that there were certain small added impurities that would cause the gas to be eliminated in larger quantities on solidification. In other words, mag-

nesium and calcium apparently disturbed the equilibrium existing between the solid alloy and the gas at the moment of solidification caused an excessive amount of gas to be liberated; also, there was considerable foundry trouble due to this. Has Mr. Bolton noticed any such condition in the alloys that he worked with?

M. G. Corson, New York, N. Y.—I am not going to discuss the practical side of Mr. Bolton's paper, and I hope that shortly Mr. Bolton will be able to produce castings with even more strength than now observed by him. The alloy which he used does not in the rolled state come below 56,000 lb. strength, and there is no reason why, if cast under good conditions, it should show much less. What I will try to do is to criticize certain statements.

Regarding gas analysis in the furnace, Mr. Bolton gives a figure of 68.6 per cent. of carbon monoxide in the gas over the metal. I do not see how that percentage would be obtained unless the work was done in an oxygen or a CO atmosphere.

In Fig. 9, the authors give a general idea of how metals crystallize which is open to criticism. The columnar crystallization is a general fact only in alpha type copper, or more generally in alloys which crystallize with the face centered cubic lattice. A beta copper alloy of any kind does not crystallize in the columnar type. The same is true with nearly all alloys which belong to the delta iron group. For instance, iron with about 10 per cent. aluminum or silicon will always be equiaxed and this columnar shape will not appear.

Tin bronzes occupy an intermediary position, but in any case they have less tendency to form columnar crystals than any other alpha alloys of copper. So while an alpha brass would form thin, long crystals reaching from the skin nearly to the center, the tin bronzes have a tendency to crystallize in small, more or less equiaxed crystals, and this applies to alloys with either 6, 8 or 10 per cent. tin.

I believe that it is due to the fact that no high-tin bronze above, even with, about 5 per cent. tin will crystallize completely as an alpha solid-solution alloy, be it either chill-cast or sand-cast. There will always be some delta present, and while I cannot account for the mechanism of its action, whenever delta appears the grain becomes rather small and equiaxed, and the boundary is not as smooth as it is in brasses or aluminum bronzes.

We have aluminum bronzes with 10 per cent. aluminum which show about 100,000 lb. ultimate strength, and still they are not good for pressure casting. High-strength brasses, of the manganese bronze type, may also show 100,000 lb. strength, and again they are not good for this purpose. Something is wrong with them, which is due to the type of crystallization. The grains are sharply defined and have a smooth boundary. The boundary substance is distributed along a small total surface; consequently it is fairly thick, and there is a substantial amount of space for gas waves to pass along them.

In tin bronzes, due to their equiaxedness and to the ragged boundary of the grain, it is far more difficult for the gas to pass, and this seems to be the reason why for many years, tin bronzes have been used in preference to other copper alloys, in spite of their higher price and their comparatively low tensile strength.

The diagram of Fig. 10 does not apply to copper-tin alloys, but even had it done so, in the case of the alloys Mr. Bolton experimented the 4 per cent. zinc and 2 per cent. lead would make it impossible to predict how they would crystallize. In other words, the diagram of Fig. 10 does not apply for this reason: if we take a horizontal cross-section of the ternary diagram we get curves where this horizontal plane crosses the solidus and the liquidus surface and if we have a composition between these curves, the one thing which we know beforehand is that the compositions of the crystals and the liquid must be always on a straight line, but we cannot foretell the composition of the crystals and the liquid for a given temperature.

The first two photomicrographs of gun metal show nothing but that there was too much distorted metal on the surface of the sample to be of any value for the purpose of illustration.

The gassed samples of Fig. 4 are shown etched. Had they been left unetched, pinholes and blowholes, and possible fissures between the grains would have been visible. The etching obliterated somewhat these features and one cannot actually tell from the photographs that the metal was gassed.

Figs. 5 and 6 do not show any unsoundness. I believe that in cases of this kind the alloy must be first well annealed, and then be shown first unetched, so as to make visible fissures or anything else which the author may want to accentuate.

H. M. St. John, Detroit, Mich.—Every foundryman who has worked with brasses and bronzes in a furnace having reducing atmosphere has experienced the particular difficulty mentioned by the authors of this paper. The peculiar discolored fracture obtained under certain conditions is unmistakable to anyone who has had experience with it. It cannot be confused with anything else.

Naturally, since this effect seemed invariably to appear when there was a reducing atmosphere, and seldom, or never, is found when there is oxidizing atmosphere in the furnace, it is not unnatural for the experimenter, or any person having this experience, to assume that the reducing atmosphere is responsible. That was the conclusion reached by the authors of this paper, and that conclusion, I think should be taken with some reservation.

The evidence given, while it all tends toward this interpretation—I have no quarrel with the evidence—is not conclusive enough to justify us in assuming that carbon monoxide is directly responsible for this condition.

Hundreds of thousands of tons of foundry brass and bronze have been melted in the normally reducing atmosphere of the arc furnace with good results. Just how much bad metal has been made under those same conditions, it is impossible to say, but I think it probably would be reasonable to say that it is something less than 1 per cent. of the total melted. It would seem a little dangerous to assume that the results we get in 1 per cent. of the cases are to govern our conclusions and to ignore the other 99 per cent.

There is a possibility, although the authors have attempted to eliminate it, that the difficulty referred to, which is a very real, serious difficulty, is due to the presence of solid metallic or nonmetallic impurities in the metal. If we assume that to be the case, we should remember next that such impurities are usually subject to oxidation. Oxidizing brass is the commonest method of refining it. We get rid of iron, aluminum and the like in that manner, and if we have such an impurity, for the sake of argument, which is giving us this particular difficulty, quite obviously when we have a reducing atmosphere in the furnace the impurity gets a full chance to work, there is no tendency to remove it, and the result is as described. On the contrary, with an oxidizing atmosphere, if the impurity is not present is too great an amount, it should be removed. That is another possible explanation of the results given.

There is a good deal of evidence to the effect that silicon is responsible for this peculiar discolored fracture.

We have had in our foundry and in our laboratory several years of experience with this shrinkage condition and have carried on a number of experiments. These I hope to describe and to bring forward the evidence in the sumposium next year. I can simply state a couple of points now. We have found in the laboratory, using virgin metal, eliminating other impurities as far as possible, that we can exactly duplicate this fracture and the microstructure shown in this paper by the addition of metallic silicon to virgin metal. It can also be duplicated by other means. It can be obtained in the foundry by the reduction of silicon, presumably from the lining

or from the foundry sands that may be mixed with the metal. It can also be obtained from silicon carbide in the lining.

There is substantial evidence to back up each one of those points. I would not say that this evidence is conclusive, but at least it is sufficiently impressive to leave the question open, and I think that as we get the papers which should follow as the result of this opening paper, we are due to learn a good deal more about it. At the moment we should simply avoid forming any too definite conclusion as to the cause of this really serious difficulty.

One point perhaps should be mentioned: yellow brass, straight copper and zinc, whether or not it contains lead, is not likely to show the structure given in the paper even if it contains silicon. It probably will show a bad surface and look as if it had aluminum in it. There may be pit holes in the surface, but in the structure itself intercrystalline fissures are not likely to be found in such an alloy.

To confirm what has been said by Mr. Spring, I would add that our experience indicates, with an alloy of approximately 85, 5, 5 and 5 composition, that the minimum silicon that would cause serious trouble is less than 0.1 per cent. With other alloys and other conditions, it might, of course, vary.

R. J. Keeley, Philadelphia, Pa. (written discussion).—This paper should be of particular interest to foundrymen who are daily confronted with porosity or shrinkage difficulties. We have had considerable experience with porous castings and our investigations confirm the conclusion reached by the authors; namely, that porosity or shrinkage may be due to a great many causes, such as slow melting furnaces, low pouring temperatures, melting under highly reducing conditions, use of charcoal on the bottom of ladles, and in the case of castings not of uniform thicknesses, the presence of phosphorus in the metal. Phosphorus retards the solidification of the metal and thereby induces shrinkage.

As this problem is of vital importance to the non-ferrous foundry industry, particularly in the manufacture of pressure castings, we believe that some research work would be advisable to study the peculiarities of fractures produced under the various conditions enumerated. In this way the cause of the difficulty may be identified and eliminated.

J. W. Bolton.—Mr. Graham spoke of our use of one type of furnace. As a matter of fact, these conclusions were equally applicable to the three types of furnace: the gas crucible type, the gas-fired open-flame furnace, and the indirect-arc furnace. The majority of the conclusions were based on extended study of one alloy, and caution is necessary in applying any generalization until other types of alloys have been experimented with. The solubility of gases, for example, could vary according to the percentage of major constituents and also because of the presence of a small amount of various impurities.

Mr. Spring calls attention to analogies in steel-casting practice and to the poling of copper. The analogy could be drawn also in the case of gray cast iron. These phenomena of microscopic cavities all seem to be interrelated. Our first key toward a solution of this non-ferrous difficulty resulted from previous knowledge of iron foundry practice.

As regards charcoal covering the metal in a furnace operating under a highly reducing atmosphere, there is a possibility that the charcoal in that case may act in a quite opposite manner from that which we might normally expect. It is obvious that in an atmosphere of carbon monoxide, charcoal is not going to be a very strong reducing agent; carbon monoxide is already present and the charcoal may serve as a mechanical blanket.

Everyone has had experience with lead alloys and they cannot be overlooked; we realize that silicon contamination has a bad effect. In our results we keep away from

silicon and even when we added silicon deliberately, we came out with only 0.03 per cent.

The remarks of Mr. Boeck regarding the lighting of gases from exudation formations are interesting, showing that reducing gases of some nature, depending on the material used, whether hydrocarbons or carbon monoxide, must be present in the metal.

Mr. Dalbey spoke of the effect of impurities in aluminum alloys. That is a matter that must be investigated before general application of this theory can be made. The results obtained in this paper apply to one shop and largely to one alloy, although we found that our conclusions seemed to be substantiated by other results, and we got like results on certain other alloys.

In so far as the gas analysis is concerned, these samples are very carefully checked. We use an Orsat and I think that most users of this instrument will recognize that our chances are of getting too little carbon monoxide in our analyses rather than too much, as the absorption power of the solution is very rapidly dissipated.

The various figures on Figs. 9 and 10 were not intended to represent exactly the alloy under consideration. They were just sketches to refresh in our minds the characteristics of crystallization of materials of solid-solution type under consideration.

As far as crystallization in this alloy and other alloys of its type is concerned, there are conditions, in some cases due to the presence of impurities and in others due to the pouring temperature, where you may have and do have equiaxcrystals. As a matter of fact, in these stronger materials we have a larger percentage of equiaxcrystals, and in materials that tend to be porous, we have a much greater percentage of columnar crystallization. Therefore, it is quite evident that the crystallization characteristics can be changed according to the foundry operation.

There was a reason for etching the photomicrographs of Figs. 1 to 8. With reference to the criticism of Figs. 1 and 2, of course, one would have to take the microscope and examine the sample to determine whether or not it was dragged. As far as Figs. 3 to 8 are concerned, we etched those in such manner that we avoided obscuring the actual occurrence of cavities by the shadows of the dentritic formations-but also the etching indicates the positions of these cavities in regard to the crystal; lization characteristics of the material. That is a point of value and interest in the substantiation of the theory herein involved. In the particular alloy that was examined here, we were very careful to keep away from the delta eutectoid.

Mr. St. John mentioned the discolored fracture, implying that its necessary associations were conditions resulting in intercrystalline fissures and porosity. We have found that that does not necessarily follow. There can be good-looking fractures from the point of view of color, and exceedingly porous metal on the test. It all depends on whether the castings are put under hydrostatic tests which discolor the metal interstices, or whether the casting is broken before the interstices are discolored.

Good results mentioned by Mr. St. John, obtained by various manufacturers, are only qualitative. To find out what is good metal and what is bad metal, the porosity test cup illustrated in the paper (which is made cut down ⅛ in. wall all over and subjected to gas pressure) will give a very severe test of alloy. The question of absolute soundness and commercial soundness are not analogous. An absolutely sound alloy is not a necessity on a pressure test. A few fissures may not ruin its engineering usefulness.

I am rather inclined to agree with Mr. St. John's warning as far as silicon is concerned, and regarding other impurities, that these may upset the conceptions drawn on a simple alloy of this type. The silicon in this particular case was kept down to a negligible percentage, so we feel that it had very little to do with the results obtained.

This paper is of a preliminary nature, and it follows the paper written by Boeck and Woyski. We must try out the simple things before we get into the more difficult.

W. A. Cowan recently presented a valuable paper[24] in which he showed that in certain systems containing eutectics, some components differ in contraction, and this phenomenon causes microscopic cavities in the metal. Thus this factor may be added to those enumerated by Mr. Weigand and myself on solid-solution alloys as one giving rise to incipient shrinkage in certain eutectic-containing alloys. Mr. Cowan has called to our attention two significant papers not mentioned in our references.[25] These are "Les Retassures Intercrystallines," by Guillet, Galibourg, and Ballay, and "Porosity and Physical Properties of Tombac (Red Brass)" as abstracted in *Continental Met. & Chem. Eng.*

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[24] W. A. Cowan: Minute Shrinkage Cavities in Some Cast Alloys of Heterogeneous Structure. *Jnl.* Inst. Met. (1928) **39,** 53.

[25] L. Guillet, J. Galibourg and M. Ballay: Les Retassures Intercrystallines. *Rev. de Mét.* (1925) **22,** 253.

Porosity and Physical Properties of Tombac (Red Brass). Abst. *Cont. Met. & Chem. Eng.* (1927) **2,** 1213.

Some Observations in Heat Treatment of Muntz Metal

By L. Russell van Wert,* Pittsburgh, Pa.

(New York Meeting, February, 1929)

During an investigation in which the solubility relations of the phases in Muntz metal (60 per cent. copper, 40 per cent. zinc) were under study, certain phenomena that had no immediate connection with the main problem were observed, which were thought sufficiently interesting to study further. Because of lack of time, only a preliminary survey was made of two of these; namely, the cleavage structure developed under certain conditions in a 60:40 brass and abnormal grain growth in this alloy.

Cleavage Structure in Heat-treated Muntz Metal

Carpenter noted many years ago that cold-working a brass of the Muntz metal type, which had been quenched previously from within the beta field, results in a partial breakdown of the supersaturated beta solution and the precipitation of the solute (the alpha solution) in the cleavage planes of the beta grains. This manner of rejection of a solute from a metastable solid solution is not peculiar to this particular alloy, for among others, it occurs in the cold-working of certain austenitic steels; for example, the austenitic nickel steels. In these ferrous alloys, cold deformation produces a partial decomposition of the austenite, with the formation of martensitic "needles" and zigzags in the austenitic polyhedra. It is interesting to note that while the two solid solutions—austenite and quenched Muntz metal— are metastable and in their mode of decomposition behave quite alike when deformed in the cold, the metastability of each results from a different cause; *viz.*, that of the austenite from the fact that it is a supercooled solution (its solvent, gamma iron, at ordinary temperatures is below its normal stable range) whereas the metastability of the quenched Muntz metal is the result of supersaturation.

When a 60:40 brass is quenched from above 800° C.—that is, from within the field where the beta phase alone is stable—this solution is retained practically intact and the alloy so cooled is found to consist almost entirely of polyhedra of this solution with only a little alpha present ordinarily at the boundaries of the beta grains—the result of a slight

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decomposition of the beta which even the rapid rate of cooling was not sufficient to completely prevent (see Fig. 1).

While ordinarily the place of greatest instability of the supersaturated beta solution occurs at the grain boundaries, on occasion some rejection of the alpha solution on quenching may occur also within the beta polyhedra. In Fig. 3 may be seen the microstructure of a quenched brass showing alpha in the cleavage planes of three of the five grains present. Obviously, then, decomposition of the beta solution is not, in all cases, confined to the boundary surfaces; it may take place, as in this instance, to some extent within the grains and, probably because of certain atomic relationships present along the cleavage planes which make for instability there, all intragranular decomposition takes place

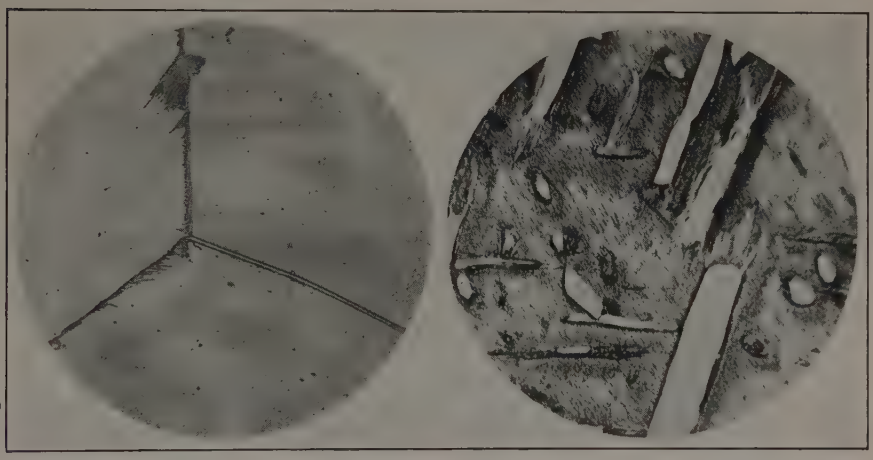

FIG. 1.—60:40 BRASS QUENCHED FROM 850° C. $NH_4OH + H_2O_2$ ETCH. × 220.

FIG. 2.—60:40 BRASS QUENCHED (H_2O) FROM 850° C. REHEATED TO 750° C. FOR ½ HR. ACID $FeCl_3$ ETCH. × 220.

along these planes. Boundary decomposition results doubtless from the same general fundamental cause and is the more frequently occurring type only because the stability of the interface between materials differently orientated is less than the stability of the cleavage plane on both sides of which lies material of the same orientation.

It is interesting to note in this connection that the parallel markings indicating the presence of the intracrystalline rejected alpha have one end, and in the smaller grains both ends, extending to the boundary. However, it is not believed that the rejection of the alpha to the boundaries preceded the rejection to the cleavage planes. That may be the case, and often is, but when intercrystalline separation precedes, in point of time, the intracrystalline, the alpha in the planes does not take on as definitely the parallel markings as is shown in Fig. 3; neither do the alpha "fingers" extend so deeply within the grains, nor are they of

constant width, naturally becoming wider as they approach the parent boundary.

The alloy of which the structure is shown in Fig. 3 was the standard 60:40 composition but carried 0.33 per cent. lead. The author has observed that lead, in amounts as small as 0.3 per cent., decreases the stability of the supersaturated beta solution. This may account for the rather unusual behavior of this particular alloy, and may be explained by the insoluble lead globules acting as nuclei initiating decomposition within the grains.

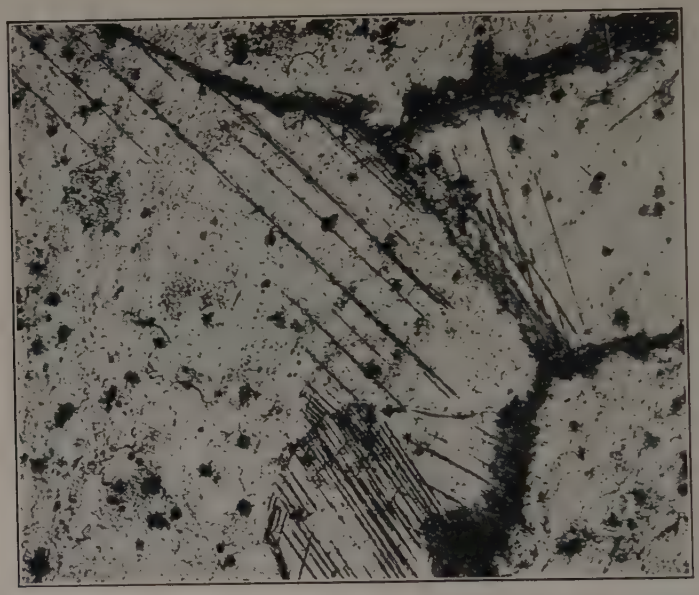

FIG. 3.—60:40 BRASS QUENCHED FROM 850° C. $NH_4OH + H_2O_2$ ETCH. × 220.

The quenched alloy, consisting of the homogeneous but metastable beta solution, on reheating to temperatures below 800° C., undergoes decomposition again with the rejection of the alpha phase but to a much larger extent than in the preceding the rejection occurs in the cleavage planes. Fig. 2 shows the structure of a quenched specimen reheated for

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FIG. 4.—SAME ALLOY AS FIG. 2, QUENCHED (H_2O) FROM 850° C. REHEATED TO 750° C. ACID $FeCl_3$ ETCH. × 220.

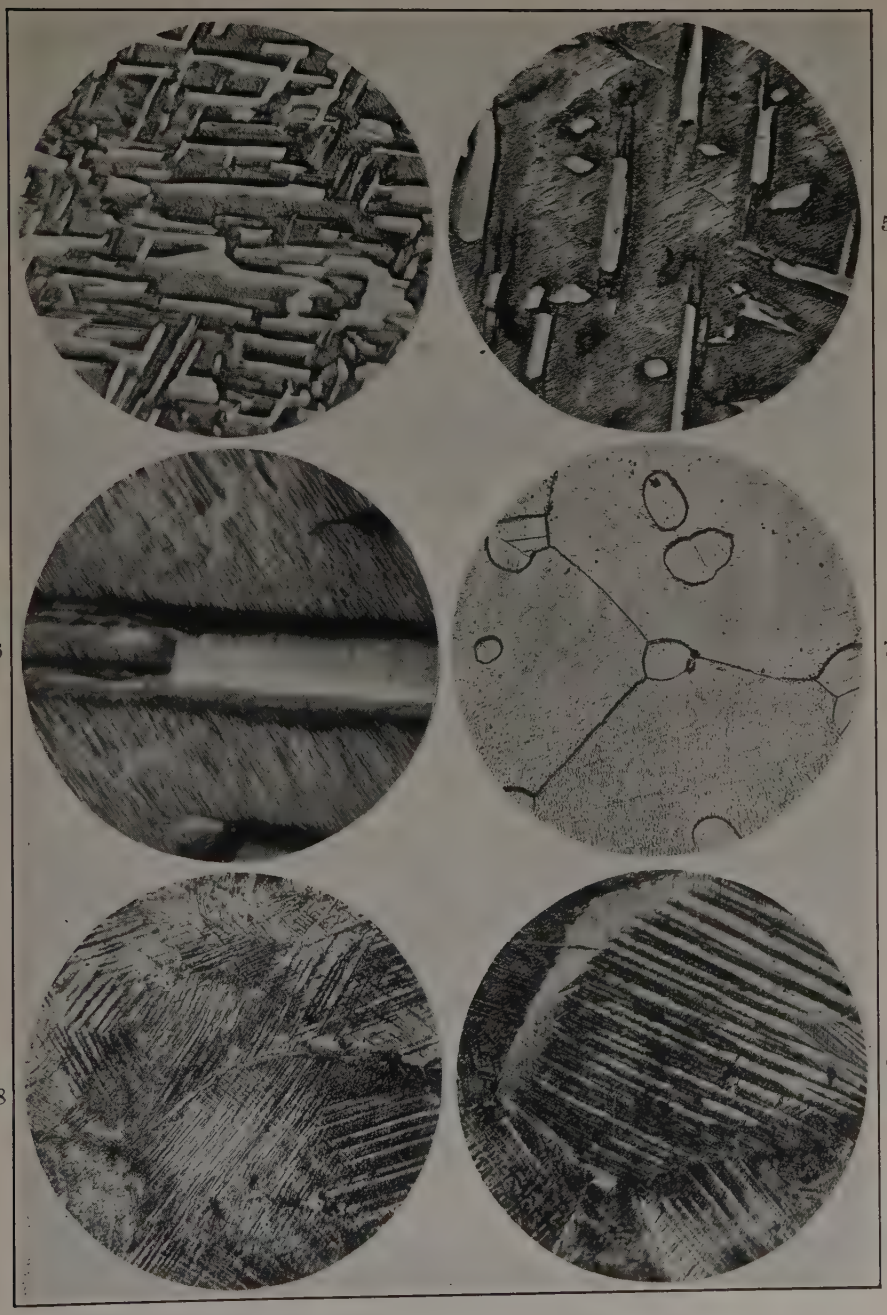
FIG. 5.—60 : 40 BRASS ALLOY QUENCHED (H_2O) FROM 850° C. REHEATED ½ HR. TO 750° C. ACID $FeCl_3$ ETCH. × 220.

FIG. 6.—ALPHA ISLAND IN ALLOY QUENCHED (H_2O) FROM 850° C. REHEATED TO 750° C. ½ HR. ACID $FeCl_3$ ETCH. × 465.

FIG. 7.—60:40 BRASS ALLOY SLOWLY COOLED FROM +800° C. REHEATED ½ HR. TO 750° C. $NH_4OH + H_2O_2$ ETCH. × 220.

FIG. 8.—60:40 BRASS ALLOY QUENCHED (H_2O) FROM 850° C. COLD-WORKED. REHEATED TO 250° C. FOR ½ HR. ACID $FeCl_3$ ETCH. × 220.

FIG. 9.—60:40 BRASS ALLOY QUENCHED FROM +800° C. COLD-WORKED. REHEATED TO 250° C. FOR ½ HR. ACID $FeCl_3$ ETCH. × 220.



FIGS. 4–9.— (CAPTIONS ON OPPOSITE PAGE.)

½ hr. at 750° C. The groundmass is the beta solution and the lighter colored, isolated areas are alpha. The general elongated character of these indicates that the alpha was precipitated in the cleavage planes. Fig. 4 gives the microstructure of the same quenched alloy reheated to 750° C. but not held at that temperature. If anything, the cleavage structure is more prominent after this shorter heating, probably on account of the smaller alpha areas (the result of lack of sufficient time for growth) obscuring less than in the preceding their mode of origin.

Fig. 5 shows the structure of another quenched alloy reheated to 750° C. These three photographs (Figs. 2, 4 and 5) show the same general tendency of the alpha solution to segregate along the cleavage planes; they also show the mechanism whereby the precipitated alpha is taken back into solution with rise in temperature. Heating a quenched alloy results (1) in the breakdown of the metastable beta solution and the precipitation of the solute preferentially in the cleavage planes of the beta; (2) when the temperature is raised sufficiently, in the re-solution of this solute. It is this process of re-solution, in an arrested stage, that is shown in Figs. 2 and 5. The temperature (750° C.) to which these alloys were reheated is only 50° C. below the point at which solution of the alpha is complete, thus at this temperature solution is rather well advanced. Obviously, then, the several rectangular alpha areas in the photomicrographs are the remnants of much larger areas; they represent alpha masses *in the process of being dissolved.*

The interesting feature of this re-solution process is its peculiar mechanism; namely, solution occurs exclusively at the ends of the rectangular areas—in other words, the alpha "islands" remain constant in width during the dissolving process and decrease in size takes place through reduction in length alone. Fig. 6 shows one of these "islands" at higher magnification (465×). This reveals clearly the way in which solution of the alpha proceeds. It is evidently the result of a less stable condition (as regards immiscibility of the two phases) at the end interfaces of the alpha masses and the beta matrix than at the lateral interfaces. This, in turn, may be the result of an enforced placement or orientation of the alpha material in the planes due to its originating in a space more constricted in one direction than in others. This possibility seems to have justification in the circumstance that "directional solubility" exists only when the alpha phase originates from a supersaturated solid solution; that is, only when it separates along the cleavage planes of the beta polyhedra. When it forms in the more usual way by a slow precipitation from a solution that is merely saturated (and when no pronounced segregation in the planes takes place), the alpha "islands" are rounded, and on reheating these are dissolved equally in all directions. Fig. 7 shows the structure of an alloy that was slowly cooled from above 800° C., then reheated to 750° C. for ½ hr. Residual alpha is present,

but unlike the alpha shown in Figs. 2 and 5, it occurs as more or less rounded masses. On the slow cooling, the alpha did not segregate to the planes and on re-solution during heating it dissolved uniformly.

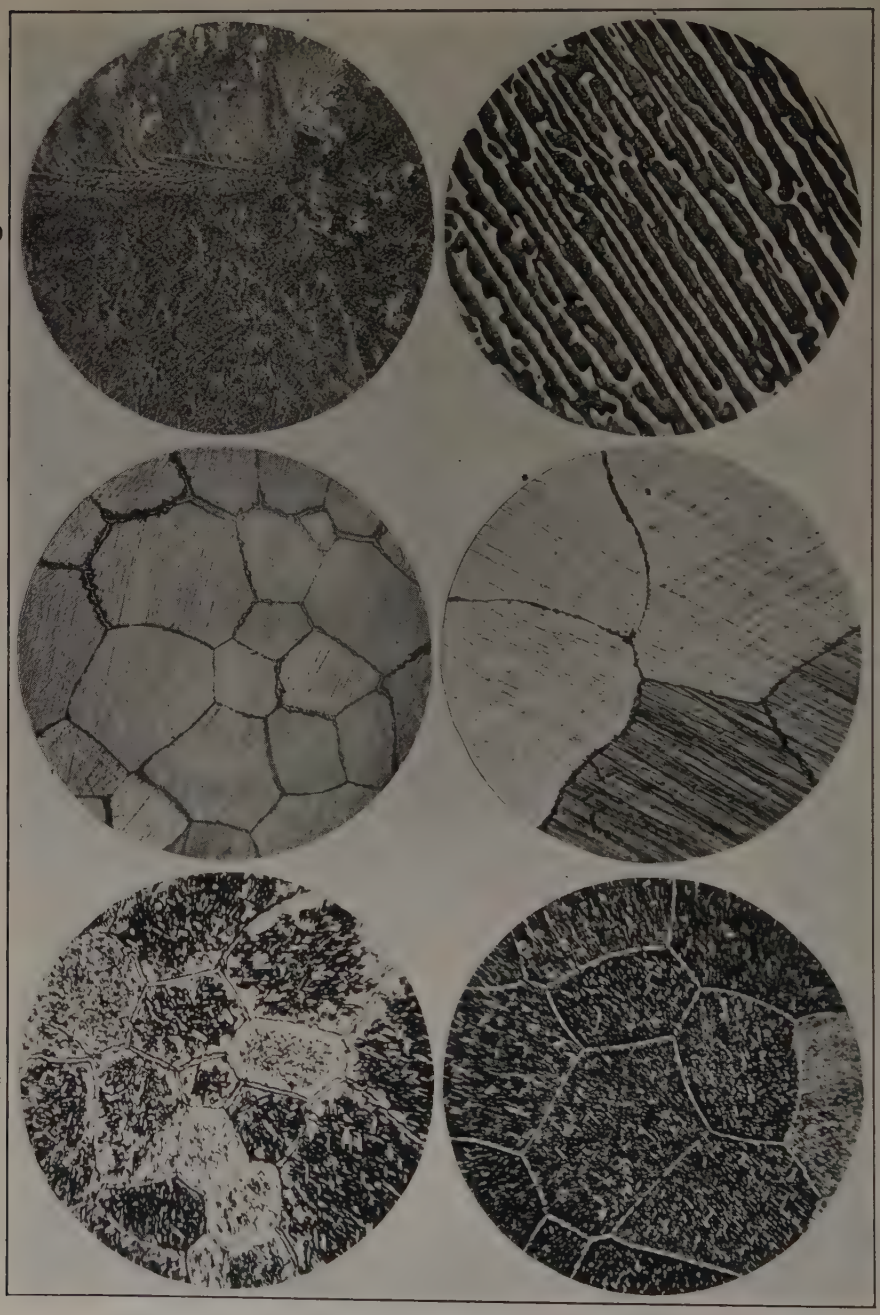
As mentioned, cold-working a quenched alloy results in the precipitation of a part of the alpha phase. It was thought quite possible to accentuate the cleavage structure on reheating by cold-working the quenched brass prior to the reheating. Figs. 8 and 9 give the structures of two specimens of such cold-worked (hammered) and reheated (to 250° C. for ½ hr.) brasses. Each specimen had been quenched from above 800° C. previous to the cold-working. The alpha phase has evidently been rejected to the slip planes produced in the cold deformation. When compared to the structure of the same alloy similarly treated, with the exception of the cold working (see Fig. 10), one sees the effect of cold deformation in the lessened stability on the reheating. Fig. 11 is the structure of another specimen developed by cold deformation followed by reheating to 500° C. for ½ hr. The higher heating produces a more decided cleavage structure.

Abnormal Grain Growth in Quenched Muntz Metal

It was observed that if a 60:40 brass, quenched from 800° C., were subsequently reheated to the beta range and quenched, the grain size was much larger than after the first heating and quenching treatment; in many instances, grain growth during reheating proceeded to so great an extent that only two or three grains, or even a single grain, occupied the entire section (1½-in. dia. round rod). Moreover, this abnormal grain growth did not occur, if the reheating temperature fell short of that necessary to redissolve all of the alpha phase; neither did the rate of heating through the 470° C. ($\beta^1 \rightarrow \beta$) transition affect grain growth.

Fig. 12 is the normal structure of a 60:40 brass quenched from 800° C. The alloy had been slowly cooled from above 800° C. before this treatment. The grains are the beta solid solution, the darker network is the alpha. Fig. 13 shows the structure of the same alloy reheated to 800° C., held at that temperature for ½ hr. and quenched. A comparison of Figs. 12 and 13 shows the large increase in grain size that occurs on the reheating. The structure of the quenched 60:40 alloy after reheating to 750° C. for ½ hr. and again quenching is given in Fig. 14. No grain growth took place at the point where some unabsorbed alpha remains, on the reheating to this lower temperature. Fig. 15 gives the structure of this alloy after a second reheating to 750° C. and a sojourn there for ½ hr. Again, no marked grain growth has occurred.

Inasmuch as the beta grains of the slowly cooled alloy exhibit no growth abnormality on reheating to the beta range, while those of the rapidly cooled (quenched) alloy do, the explanation of the excessive



FIGS. 10–15.—(CAPTIONS ON OPPOSITE PAGE.)

grain growth in the latter must apparently be sought in the somewhat (assumed) strained condition of the beta phase in the quenched alloy, which on reheating to 800° C. induces an excessive grain growth. As to the failure to develop an abnormal growth of grain in the quenched alloys reheated to 750° C., (Figs. 14 and 15), apart from the lower temperature involved, which in itself may account for the lessened tendency for growth, it is probably true also that the numerous scattered islets of residual alpha act as inhibitors to growth. At least, on the complete disappearance of the alpha, at but 50° C. higher, marked growth in the strained (?) beta occurs.

DISCUSSION

A. J. Phillips, Waterbury, Conn.—The author quotes Carpenter to the effect that beta brass when cold-worked partly breaks down by the precipitation of alpha along cleavage planes. Unfortunately he does not give the reference and I have been unable to find it in a rather hurried search. I wonder if it is not possible that these "needles" referred to are mechanical twin bands rather than precipitated alpha.

In my experiments with beta brass I have found "needles" appearing upon cold working but they were not even suggestive of precipitated alpha and resembled more Neumann bands in iron. Professor Mathewson[1] has recently proved that Neumann bands in body-centered cubic iron are indeed twin bands and it is natural to assume that similar bands in body-centered cubic beta brass are also twin bands.

I believe that the fine lines shown in Fig. 3 of Mr. Van Wert's paper are due essentially to mechanical twinning as a result of contraction strains set up in quenching. While the needles do not contain alpha when first formed, conditions are such that alpha will immediately precipitate along them if the quench is delayed or if a secondary heat treatment is resorted to.

Fig. 16, which I have prepared, shows naval brass quenched from 800° C. in hot oil. The large dark areas are unquestionably precipitated alpha, but the fine needle-like areas, I believe, are mechanical twins, possibly caused by the strains set up in the precipitation of the alpha. Fig. 17 shows one of these areas at a higher magnification and Fig. 18 shows the influence of these needles on the precipitation of alpha. This is further shown by Fig. 19 at a lower magnification.

Fig. 20 shows a specimen very actively quenched from the beta range and reheated for several hours at 300° C. The preponderance of twinned alpha crystals in the

[1] C. H. Mathewson and G. H. Edmunds: The Neumann Bands in Ferrite. Iron and Steel Technology in 1928. A. I. M. E.

Fig. 10.—Same alloy as Fig. 9 quenched from +800° C. Reheated to 250° C. $NH_4OH + H_2O_2$ etch. × 220.

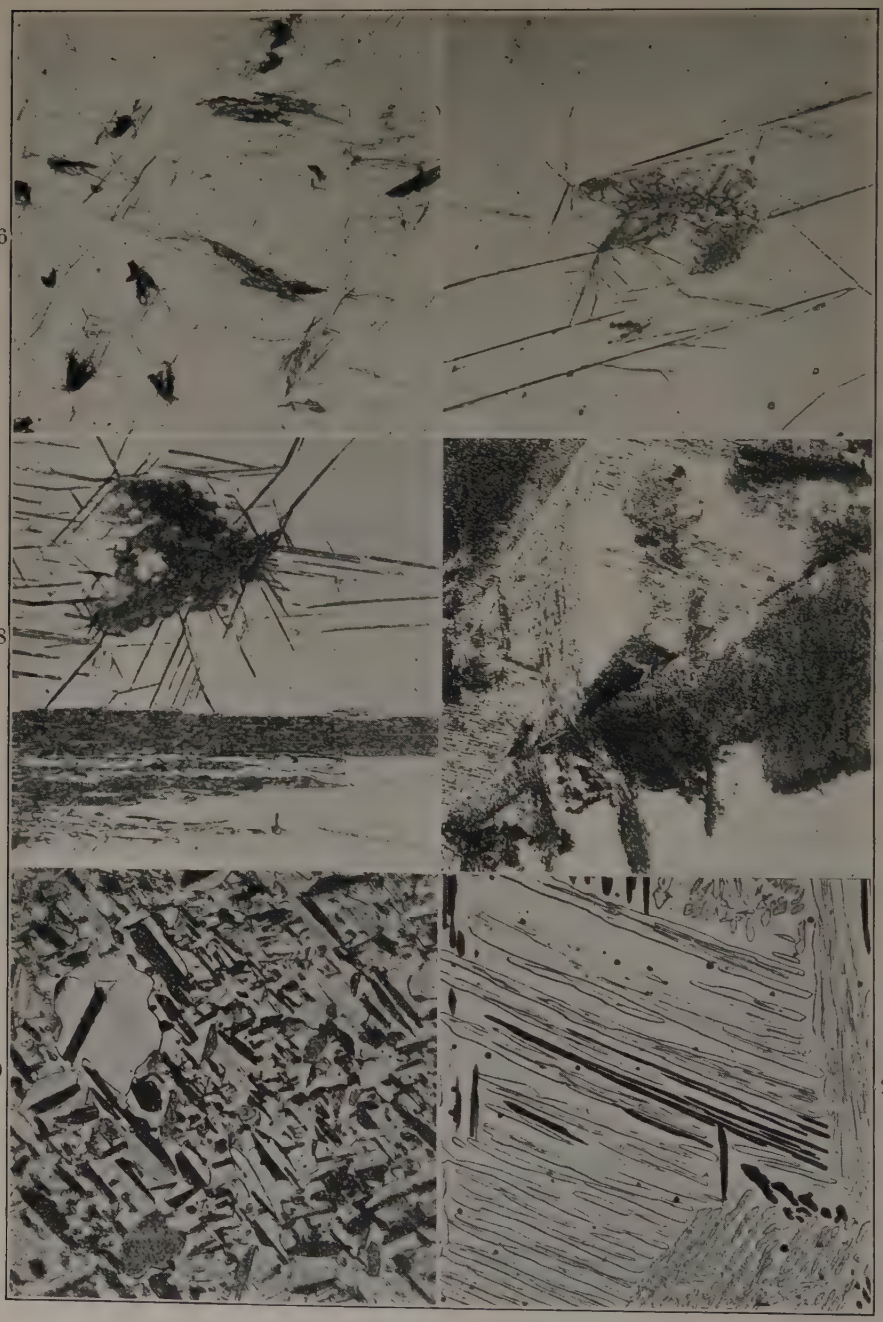
Fig. 11.—60:40 brass alloy quenched (H_2O) from +800° C. Cold-worked. Reheated to 500° C. for ½ hr. Acid $FeCl_3$ etch. × 220.

Fig. 12.—Normal structure of 60:40 brass quenched (H_2O) from 800° C. $NH_4OH + H_2O_2$ etch. × 11.

Fig. 13.—Same alloy as Fig. 12 quenched (H_2O) from 800° C. Reheated to 800° C. for ½ hr. $NH_4OH + H_2O_2$ and acid $FeCl_3$ etch. × 11.

Fig. 14.—Same alloy as Fig. 12 quenched (H_2O) from 800° C. Reheated to 750° C. for ½ hr. Acid $FeCl_3$ etch. × 11.

Fig. 15.—Same alloy as Fig. 12 quenched (H_2O) from 800° C. Reheated to 750° C. for ½ hr., quenched and reheated to 750° C. for ½ hr., and quenched. Acid $FeCl_3$ etch. × 11.



FIGS. 16–21.—(CAPTIONS ON OPPOSITE PAGE.)

specimen indicates, to my mind, that the mechanism of precipitation is such that only certain alpha orientations can be produced in any crystal. It further suggests that along any crystal plane possibly only two orientations, showing a twinned relationship to each other, can be produced. Fig. 21 is of a specimen heated to 650° C., and shows this preponderance of only a few orientations. It should be noticed that certain straight bands of alpha are light while others, parallel to them, are dark, immediately suggesting a twinned relationship.

F. H. Clark, New York, N. Y.—I agree entirely with Dr. Phillips regarding Fig. 3. Twins are often visible in quenched 60:40 brass with the beta structure and are due to the fact that the beta is unstable. Possibly the shock of the polishing operations may have aided in the formation of the twins. These mechanical twins, or Neumann bands, at about 3000 dia. magnification, show distinct parallel markings that could never be confused with the fine structure of alpha, which we sometimes call sorbite because it resembles sorbite in steel.

In regard to Figs. 8 and 9, I might say to Dr. Phillips that the structure of the cold-worked beta simply shows the large beta grains loaded with slip bands due to the cold working. On reheating below 470° C., the alpha is precipitated as Mr. Van Wert has shown in Figs. 8 and 9. This structure was shown in a paper which I presented at the Institute two years ago.[2]

[2] F. H. Clark: A Study of the Heat Treatment, Microstructure and Hardness of 60:40 Brass. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 276.

Fig. 16.—Naval brass, quenched from 800° C. in oil at 150° C. × 100.
Fig. 17.—Naval brass, quenched from 800° C. in oil at 150° C. × 500.
Fig. 18.—Naval brass, quenched from 800° C. in oil at 150° C. × 500.
Fig. 19.—Naval brass, quenched from 800° C. in oil at 150° C. × 100.
Fig. 20.—Naval brass, quenched from 750° C. in ice water and reheated to 300° C. × 500.
Fig. 21.—Naval brass, annealed at 650° C. × 100.

All etched with $NH_4OH + H_2O_2$

High-strength Brasses

By O. W. Ellis,* East Pittsburgh, Pa.

(New York Meeting, February, 1929)

Recently there has been a considerable revival of interest in the effects of the various elements commonly added to brass for the purpose of increasing its strength. For many years the work of Guillet[2]† alone gave reliable information in this regard. Even today his determinations of the coefficients of equivalence of the various elements relative to zinc in brass are those universally employed in industry. This is so because these coefficients have stood the test of time—their substantial correctness has been proved in almost universal practice.

It is not our intention to discuss here these coefficients or their use. Rather do we wish to emphasize the need for further systematic studies of the mechanical properties of the ternary systems of copper, zinc, and other individual elements. Since Guillet published the results of his first investigations Millington,[16] Smalley[33] and Thibaud[45] have added somewhat to our information. In general they have confirmed the findings of Guillet, which may be stated in the following rather general terms:

1. The addition of aluminum to the 70:30 and 60:40 brasses progressively increases their hardness and strength and reduces their ductility and resistance to shock.

2. The addition of small amounts of iron to a 60:40 brass improves its strength without affecting its ductility.

3. The addition of small amounts of manganese to a 60:40 brass causes a progressive increase in its strength and reduction in its ductility.

A considerable amount of information has been amassed in regard to the effect of nickel on brass (9, 22, 41) which it is unnecessary to refer to here, in view of the scope of this paper.

The situation in regard to these alloys in 1926 was very clearly stated by an anonymous writer,[47] in *The Metallurgist* of February of that year, whose remarks were so to the point that they are well worth quoting:

> It will be seen that there are still large fields remaining to be studied in each of these systems (*those of the aluminum, iron, nickel and manganese brasses*) before our knowledge is adequate.
>
> When we come to the more complicated systems the position is even less satisfactory, and on account of the very incomplete nature of the work which has been

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† Superior figures refer to bibliography at end of paper.

TABLE 1.—*Summary of Results on High-strength Brasses*

Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Iron, Per Cent.	Nickel, Per Cent.	Manganese, Per Cent.	Ultimate Stress, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
Aluminum-iron Brasses—Smalley[48]							
59.1	37.31	2.96	0.61			90,500	19.0
59.0	37.0	3.0	1.00			96,900	26.0
59.15	35.96	3.02	1.87			96,200	20.5
Aluminum-nickel Brasses—Smalley[48]							
58.88	36.51	1.43	0.10	3.08		69,000	34.0
55.60	39.38	1.64	0.11	3.27		77,700	15.0
60.50	33.65	2.89		2.96		82,200	19.0
69.42	21.78	4.93	0.10	3.77		76,000	13.0
Aluminum-manganese Brasses—Smalley[33]							
59.45	35.85	0.98	0.22		3.49	71,200	25.0
58.15	35.18	2.24	0.25		4.10	90,800	14.0
57.23	37.90	2.59	0.20		2.08	92,700	18.0
58.87	37.13	2.94	0.10		0.96	86,700	11.0
59.34	35.34	3.10	0.20		2.02	96,200	15.0
58.32	34.54	3.12	0.10		3.92	101,500	13.0
58.76	35.16	1.95	0.20		3.43	88,700	13.0
Iron-nickel Brasses—Guillet[26]							
50.13	48.80		0.49	0.58		24,600	3.0
50.60	46.71		1.33	1.36		59,600	14.0
50.60	43.85		2.83	2.72		76,500	20.0
52.58	38.41		4.08	4.93		57,600	17.0
54.52	43.73		0.77	0.98		56,700	14.5
55.78	40.93		1.36	1.93		61,400	43.0
56.19	39.60		2.09	2.12		60,900	50.0
56.55	33.37		5.48	4.60		26,000	1.0
Iron-manganese Brasses—Guillet[26]							
55.14	42.53		1.23		1.10	51,500	13.5
58.52	35.52		1.76		4.20	36,300	6.6
60.32	38.54		0.59		0.35	51,500	47.0
60.47	37.11		1.27		1.15	52,000	47.0
60.94	35.17		1.59		2.30	47,700	28.0
63.21	30.80		1.74		4.25	Brittle	
Aluminum-iron-nickel Brasses—Smalley[48]							
60.02	31.45	4.10	1.45	3.0		99,700	12.0
Iron-nickel-manganese Brasses—Thibaud[45]							
57.5	35.2		0.3	5.0	2.0	89,600	32.0
59.67	32.73	3.30	2.25		2.05	98,000	13.5
58.11	34.31	1.95	1.65		3.98	94,800	14.0
58.74	36.61	1.60	1.22		1.83	81,800	19.0
59.45	36.60	1.56	0.4		1.97	80,400	22.0
Aluminum-iron-nickel-manganese Brass—Thibaud[45]							
56.0	36.5	1.5	1.5	3.0	1.5	96,400–100,800	20–25

Superior figures refer to bibliography at end of paper.

done, it will be more convenient to show the results which have been obtained in the form of a table (Table 1).

The complexity of these systems and the absence of any constant relations between the various series render a detailed discussion of the results impossible. It may be useful, however, to draw attention to two facts. In the first place, the table, which represents most of the systematic work, the results of which have been published, illustrates the very incomplete nature of our present knowledge of these complex brasses. If we take the iron-nickel brasses as an example, it will be noticed that the recorded work deals with only two series, one in which the copper is kept constant at about 50 per cent., while the iron and nickel are increased equally at the expense of the zinc; and the other in which the iron and nickel are increased in the same way, while the copper remains constant at 55 per cent. We know nothing of the effects of similar additions to 70:30 and 60:40 brasses, nor of varying only the nickel or the iron; nor, again, of replacing the copper instead of the zinc. This one example serves to indicate the vast amount of work which must still be done before our knowledge of the effects on cast alloys of even these four metals can be said to be sufficient. Even then the rolling properties and the effects of heat treatment remain to be studied.

Another fact which emerges from the figures is that the complexity of the alloys recommended by Thibaud does not seem to be justified by their properties as compared with those of simpler alloys. It will be seen, for example, that the brass containing aluminum, iron, nickel, and manganese has an ultimate stress only very slightly greater than that of a brass containing only aluminum and iron, while its elongation is actually less. It would seem, therefore, that a systematic study of the simpler systems, and particularly that containing aluminum and iron, would yield more profitable results than haphazard work on the more complicated alloys.

Present Investigation

There can be no doubt that these criticisms were fully deserved. However, it should be noted that a majority of those interested in the development of these alloys recognized the existence of these unsatisfactory conditions and were preparing to set them right. In this connection the author himself has carried out a somewhat extensive investigation which, though failing to satisfy the requirement that the ternary systems be first examined, goes some way in extending our knowledge of the relative effects of the elements aluminum, iron, manganese and tin on the mechanical properties of alpha-beta and beta brass. The investigation may be considered as divided into two parts. In the first part the author made a preliminary survey of these complex alloys with the view of determining the effect of tin. The use of tin he felt to be unnecessary, if not absolutely objectionable; first, on account of its cost, and second, on account of the very small proportions that were required to cause the appearance of the harmful delta constituent in many of these alloys. In the second part the author confined his attention to brasses free from tin and containing varying amounts of the other metals already referred to.

In both parts of the investigation the conditions of melting and pouring were the same. The charges comprised high-conductivity

copper, Horsehead zinc, aluminum of the usual commercial quality, electrolytic iron, metallic manganese and Straits tin. The copper was in all cases melted first. To the molten copper the iron was added and, when it had completely dissolved, this being ascertained by careful observation of the melts, the manganese was introduced. This was followed by the aluminum and tin. The crucible (Acheson graphite) was now removed from the furnace, the zinc being added to the melt outside the furnace. The melt was well stirred and finally was poured into a chill mold at a measured temperature of 980° C. to 1020° C. The mold was of iron, approximately 4 in. long, 3 in. deep and 2¾ in. wide, and was suitably tapered to enable the ingots when made to be readily stripped from the mold, but it was coated with a lime wash before use. The lesser transverse cross-section of the ingots, which weighed about 10 lb. apiece, agreed with that referred to in the Tentative Specification for Manganese Bronze Ingots for Sand Casting of the A. S. T. M. B7–27. The ingots, however, were only about one-third the length of the A. S. T. M. ingot and, hence, one-third the weight. Their rates of cooling, however, would differ but slightly from those of ingots cast in the standard mold. Hence, also, their mechanical properties would not differ materially from those of alloys cast in the form of A. S. T. M. ingots. The A. S. T. M. specification, it may be observed, requires the following minimum properties of material cast in the standard mold: tensile strength, 70,000 lb. per sq. in.; elongation in 2 in., 30 per cent.

TABLE 2.—*Analyses and Mechanical Properties of Brasses Containing Tin*

Number	Cu, Per Cent.	Zn, Per Cent. (Diff.)	Al, Per Cent.	Fe, Per Cent.	Mn, Per Cent.	Sn, Per Cent.	Prop. Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. Per Cent.	Elong. in 2 In., Per Cent.	Red. of Area, Per Cent.	Hardness Number*
8	56.81	40.51	1.12	0.34	0.74	0.48	21,000	34,200	84,750	21.5	21.7	73
9	56.45	41.13	0.66	0.42	0.80	0.54	18,000	32,400	77,850	22.3	22.2	72
10	56.65	39.54	1.10	0.40	0.80	1.51	26,000	N. O.	70,650	3.0	4.3	77
11	56.89	40.36	0.63	0.11	0.60	1.41	27,000	43,000	83,800	16.3	17.5	74
12	56.73	39.72	1.16	0.31	1.65	0.43	24,000	38,250	89,150	23.8	24.1	74
13	56.96	40.46	0.49	0.17	1.56	0.36	20,000	34,500	81,925	21.0	22.1	72
†												
14	56.48	38.99	0.47	0.73	1.73	1.64	30,000	49,000	91,750	21.0	21.7	76
15	57.06	39.74	0.97	0.95	0.82	0.46	21,500	35,327	87,600	29.8	28.0	73
16	56.76	40.52	0.51	0.95	0.80	0.46	17,000	29,500	80,250	38.0	35.9	69
17	57.12	38.78	0.99	0.79	0.76	1.56	28,000	48,000	94.375	22.3	23.4	76
18	57.15	39.37	0.47	0.70	0.72	1.59	17,500	38,000	85,250	27.0	26.7	73
19	56.60	39.77	0.93	0.81	1.59	0.30	21,000	37,250	75,125	10.0	11.5	74
20	56.87	39.83	0.46	0.84	1.62	0.38	15,000	28,500	83,150	20.0	22.9	69
21	56.90	38.10	0.95	0.95	1.50	1.60	30,000	52,600	92,500	14.0	14.5	77
22	56.60	38.99	0.47	0.73	1.65	1.56	19,000	43,375	85,175	16.4	17.4	74

* Rockwell.

† Alloy No. 7 would have come in here had its analysis been correct.

Results of Part 1 of Author's Investigation

In Table 2 are given the analyses and mechanical properties of the first group of alloys, those containing tin. In this table the alloys are arranged in pairs in such a way that the effect of aluminum may be roughly determined. Reference to the analyses will show that in all cases the alloys having even numbers contain a greater amount of aluminum than those having odd numbers. The amount of aluminum in the former alloys is about twice as much as that in the latter. There are obvious differences in the proportions of the other elements in these alloys, so that it is impossible from an examination of one pair of alloys to determine the exact effect of aluminum. Nor can this be accurately determined from the results of the tests as a whole, the number of tests being insufficient to make possible the elimination of the effects of the variations in elements other than aluminum so as to enable a categorical statement to be made as to the effect of aluminum. The averaging of the differences between the results of even these few tests is, nevertheless, sufficient to guide one to a fairly reasonable view of the general effect of aluminum on these alloys, as is shown in Table 3.

Table 3.—*Differences between Results of Tests Listed in Table* 2

	Differences in Percentages of Elements						Changes in Properties					
	Cu	Zn	Al	Fe	Mn	Zn	A	B	C	D	E	F
8 minus 9	+ 0.36	− 0.62	+ 0.46	− 0.08	− 0.06	− 0.06	+ 3,000	+ 1,800	+ 6,900	− 0.8	− 0.5	− 1.20
12 minus 13	− 0.23	− 0.74	− 0.67	+ 0.14	+ 0.09	+ 0.07	+ 4,000	+ 3,750	+ 7,225	+ 2.8	+ 2.0	+ 2.10
15 minus 16	+ 0.30	− 0.78	+ 0.46	nil	+ 0.02	nil	+ 4,500	+ 5,827	+ 7,350	− 8.2	− 7.9	+ 4.05
17 minus 18	− 0.03	− 0.59	+ 0.52	+ 0.09	+ 0.04	− 0.03	+ 10,500	+ 10,000	+ 9,125	− 4.7	− 3.3	+ 2.40
21 minus 22	+ 0.30	− 0.89	+ 0.48	+ 0.22	− 0.15	+ 0.04	+ 11,000	+ 9,225	+ 7,325	− 2.3	− 2.9	+ 2.85
Sums of differences	+ 0.70	− 3.62	+ 2.59	+ 0.37	− 0.06	+ 0.02	+ 33,000	+ 30,602	+ 37,925	− 13.2	− 12.6	+ 12.6

A = Limit of proportionality, lb. per sq. in.
B = Yield point, lb. per sq. in.
C = Tensile strength, lb. per sq. in.
D = Percentage elongation.
E = Reduction of area, per cent.
F = Rockwell hardness number, B scale; $\frac{1}{8}$-in. ball; 100-kg. load.

By dividing the values quoted in the bottom row of Table 3, which represent the sums of the numbers in the columns above these values, by 25.9 (10 times the sum of the differences in aluminum) the approximate effect of 0.10 aluminum upon the properties of a complex brass containing approximately 57 per cent. of copper may be obtained. The result of this operation is as follows:

EFFECT OF 0.10 PER CENT. OF ALUMINUM

Difference in percentage:

Of copper	= 0.027+
Of zinc	= 0.140−
Of iron	= 0.014+
Of manganese	= 0.002−
Of tin	= 0.001+

Limit of proportionality	+1280 lb. per sq. in.
Yield point	+1180 lb. per sq. in.
Tensile strength	+1460 lb. per sq. in.
Elongation	−0.51 per cent.
Reduction of area	−0.49 per cent.
Rockwell hardness	+0.49

In Table 3, reference to alloys 10, 11, 19, and 20 is omitted, because alloys 10 and 19 were unsatisfactory. With the former, the test results were obviously affected by the structure of the alloy, the alpha constituent in which was present in the form of thin envelopes surrounding the grains of the beta constituent; with the latter, both test samples were distinguished by flaws which had quite clearly influenced the test results.

The number of tests has been insufficient to eliminate the effect of the substitution of copper, iron, manganese, and tin for zinc. As far as copper (0.027+) and iron (0.014+) are concerned, we know that they would tend to increase the proportion of alpha constituent and thus to soften the brass. Manganese (0.002−) would have little effect on the structure, but would slightly increase the hardness of the brass; tin (0.001+) would definitely harden the brass and reduce its alpha content. In the light of this knowledge, then, it can be said that the effect of aluminum would be somewhat more powerful than is indicated. In other words, 0.10 per cent. of aluminum would increase the strength and hardness of brass a little more than is shown above and would concurrently and, possibly, proportionately decrease its ductility.

By retabulating the alloys in such a way as to emphasize the average effect of iron upon the structure and properties of these alloys the following results have been obtained:

EFFECT OF 0.10 PER CENT. OF IRON

Difference in percentage:

Of copper	= 0.031+
Of zinc	= 0.121−
Of aluminum	= 0.021−
Of manganese	= 0.007+
Of tin	= 0.007+

Limit of proportionality	−940 lb. per sq. in.
Yield point	−670 lb. per sq. in.
Tensile strength	+ 50 lb. per sq. in.
Elongation	+1.06 per cent.
Reduction of area	+0.93 per cent.
Rockwell hardness	−1.42

For manganese the following results have been obtained:

EFFECT OF 0.10 PER CENT. OF MANGANESE

Difference in percentage:	
Of copper	= 0.012−
Of zinc	= 0.087−
Of aluminum	= 0.007−
Of iron	= 0.008+
Of tin	= 0.001−

Limit of proportionality	+180 lb. per sq. in.
Yield point	+400 lb. per sq. in.
Tensile strength	+330 lb. per sq. in.
Elongation	−0.59 per cent.
Reduction of area	−0.58 per cent.
Rockwell hardness	+0.01

It seems that, although manganese has no appreciable effect on the structure of these alloys, it has a definite influence upon their hardness and strength. The fact that alterations in the mechanical condition of these alloys apparently can be occasioned by varying their content of manganese without causing change in their structure is one of the utmost importance. For this reason, if for no other, manganese appears to deserve a position in any specification for high-tensile brasses.

The effect of tin on the properties of these alloys is indicated below:

EFFECT OF 0.10 PER CENT. OF TIN

Difference in percentage	
Of copper	= 0.018+
Of aluminum	= 0.002−
Of zinc	= 0.116−
Of iron	= 0.006−
Of manganese	= 0.006+

Limit of proportionality	+ 690 lb. per sq. in.
Yield point	+1400 lb. per sq. in.
Tensile strength	+ 680 lb. per sq. in.
Elongation	−0.64 per cent.
Reduction of area	−0.51 per cent.
Rockwell hardness	+0.42

Tin has less effect upon the structure—that is, in so far as the proportion of alpha constituent alone is concerned—than has aluminum, which is similar to it in its general influence. It is not so powerful as aluminum in its effect on the hardness and strength of these alloys but it is somewhat more potent in its influence on their ductility. In view of these facts and of its deleterious influence on the structure of these alloys, it appears that tin might well be discarded from these alloys. A further point which favors such action is the high price of the metal.

It is of interest to note that such a view must have been arrived at independently by other workers in this field, who, though they make no

statement in this regard, have in most cases omitted tin from the alloys they have investigated.

Results of Part 2 of Author's Investigation

The analyses and mechanical properties of the second group of alloys are quoted in Table 4.

Table 4.—*Analyses and Mechanical Properties of Second Group of Alloys*

Number	Cu, Per Cent.	Fe, Per Cent.	Al, Per Cent.	Mn, Per Cent.	Elect. Res., Microhms per. Cm. Cube	Prop. Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Red. of Area, Per Cent.
44	56.41	0.23	0.47	0.94	10.1	15,000	24,700	75,200	25.1	26.8
45	56.25	0.07	0.51	1.78	13.1	17,900	28,400	78,800	25.9	21.7
46	56.66	0.12	0.50	3.57	20.[illegible]	20,100	31,800	79,400	27.2	24.7
47	57.33	0.07	0.88	0.94	10.4	17,300	27,500	77,600	23.7	22.1
48	56.32	0.04	0.93	1.84	13.8	20,800	30,700	83,300	26.7	20.8
49	56.68	0.07	0.93	3.55	20.3	24,500	37,600	84,800	20.1	19.9
50	56.94	0.07	1.43	1.00	10.9	19,900	30,000	85,800	24.9	23.9
51	56.15	0.07	1.42	1.83	14.3	20,900	34,100	89,200	25.9	22.9
52	57.44	0.07	1.54	3.67	21.4	33,800	39,200	92,300	16.4	18.4
17	56.15	1.04	0.38	0.84	10.1	15,600	24,300	78,300	35.1	31.4
53	56.04	0.90	0.52	1.78	14.1	19,100	27,900	69,900	19.0	21.5
54	55.29	1.12	0.50	3.58	20.4	20,500	35,200	79,600	21.5	21.9
20	56.14	0.90	0.93	0.87	10.1	16,800	26,800	85,900	34.0	31.8
21	56.50	1.07	0.88	1.83	14.3	22,100	31,400	86,600	35.9	32.3
22	57.07	1.07	0.94	3.64	22.1	22,300	33,900	80,800	25.5	23.7
55	56.35	1.12	1.73	0.91	11.1	20,900	34,600	89,200	21.4	21.1
24	56.47	1.21	2.10	1.80	14.4	23,300	36,000	95,600	34.1	31.0
56	57.10	0.60	1.72	3.71	22.5 (est.)	27,500	51,000	97,600	19.9	18.2
57	56.35	2.08	0.41	1.01	11.3	10,800	22,300	71,200	38.2	36.2
27	57.27	1.43	0.53	1.73	14.6	15,300	23,800	71,400	46.0	38.5
59	57.19	2.11	0.41	3.83	23.4	17,500	24,000	65,300	26.7	25.7
60	57.00	2.11	0.91	0.96	11.5	16,000	26,900	78,500	40.2	41.8
61	56.90	1.78	0.86	1.91	15.3	16,800	30,300	75,500	22.7	24.1
62	56.73	1.84	0.94	3.76	23.1	18,800	35,100	83,200	27.7	26.0
63	56.30	1.84	1.77	0.99	11.5	21,000	30,500	93,900	28.6	28.2
64	57.11	2.06	1 89	1.90	14.9	26,500	43,500	95,500	24.5	24.5
65	56.52	1.86	1.84	3.81	20.4	30,700	50,700	95,200	16.1	17.6
35	57.05	3.80	0.51	0.99	12.3	14,300	22,200	66,800	54.3	49.7
36	56.74	3.51	0.54	1.69	15.5 (est.)	12,500	23,500	67,500	35.0	32.1
37	56.64	3.87	0.61	3.53	23.1 (est.)	15,000	30,000	70,300	48.0	40.7
38	57.52	4.12	0.91	1.01	12.8	14,900	24,300	70,300	48.2	42.8
39	56.72	3.90	0.95	1.77	15.6	14,600	26,100	73,900	47.4	41.4
40	58.36	4.01	1.01	3.67	24.9	15,600	25,900	69,100	40.7	35.3
41	56.76	3.93	1.41	0.97	13.3 (est.)	17,500	33,200	88,500		19.2
68	56.27	4.45	1.94	2.01	16.3	24,100	45,300	86,400	11.6	15.1
69	56.05	3.87	1.82	3.80	23.2	23,600	50,300	99,500	21.1	33.1

In this table are also quoted values for the electrical resistivities of these alloys in microhms per cubic centimeter (see column 6).

In Table 4 the analyses of these alloys are arranged in groups of three. The attempt was made to keep the proportions of copper, iron, and aluminum of these groups as nearly constant as possible, but these proportions were varied from group to group, as outlined below. Within each of these groups the manganese was varied systematically. If the groups be considered in order it will be seen that in the first, fourth, seventh, and tenth groups the copper and aluminum were kept constant, while the iron and manganese were varied. Considering the first, second, and third groups alone, it will be seen that the copper and iron have been kept constant, while the aluminum and manganese have been varied. This was true also of the fourth, fifth, and sixth groups, and so on.

It is possible, by suitably choosing the alloys referred to in Table 4, to arrange them in such a way that the effect of any element on the properties of the alloys may be roughly determined, as was done in the case of the alloys containing tin (see Table 2). It is unnecessary, however, to go to this trouble. If, for example, it is desired to determine the effect of aluminum on these complex brasses, what is required is to obtain the average of the properties of the alloys containing an average of 0.49 per cent. of aluminum (see Table 4), that of the alloys containing an average of 0.92 per cent. of aluminum (see Table 4), and that of the alloys containing an average of 1.72 per cent. of aluminum (see Table 4), as is done below:

	Averages		
Aluminum	0.49	0.84	1.72
Copper	56.50	56.94	56.62
Iron	1.69	1.75	1.76
Manganese	2.11	2.15	2.20
Electrical resistivity	15.7	16.2	16.2
Proportional limit, lb. per sq. in.	16,100	18,400	24,200
Yield point, lb. per sq. in.	26,500	29,700	39,800
Tensile strength, lb. per sq. in.	72,800	79,100	92,400
Elongation, per cent	33.5	32.7	22.2
Reduction area, per cent	30.9	30.2	22.7

Then, if the values for tensile strength, for example, are plotted against aluminum content (Fig. 1) they lie close to a straight line having for its origin the value 65,500 lb. per sq. in. tensile strength and the conclusion is reached that 0.49 per cent. aluminum increases the strength of a complex brass containing about 56.58 per cent. copper from about 65,500 lb. per sq. in. to about 72,800 lb. per sq. in., or by 7300 lb. per sq. in. For the other percentages of aluminum the following values hold:

Aluminum, Per Cent.	Total Increase, Lb. per Sq. In.
0.49	7,300
0.92	13,600
1.72	23,900

These values may be used in the preparation of a curve designed to show the quantitative effect of aluminum on the strength of a complex brass and such a curve is shown in Fig. 2, which, however, extends over a wider range, having as its basis the results of work on the effect of

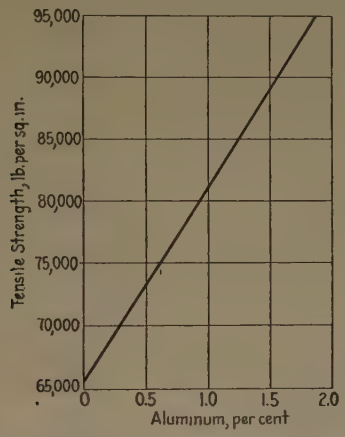

FIG. 1.—EFFECT OF ALUMINUM ON TENSILE STRENGTH OF COMPLEX BRASS.

aluminum on various brasses by the author, by Smalley,[33] by Millington,[16] and by Guillet.[2] The effect of aluminum on the percentage elongation of brass is shown in Fig. 3, this curve having been arrived at by similar means.

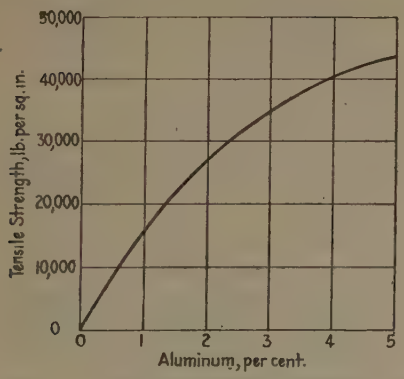

FIG. 2.—QUANTITATIVE EFFECT OF ALUMINUM ON TENSILE STRENGTH OF COMPLEX BRASS.

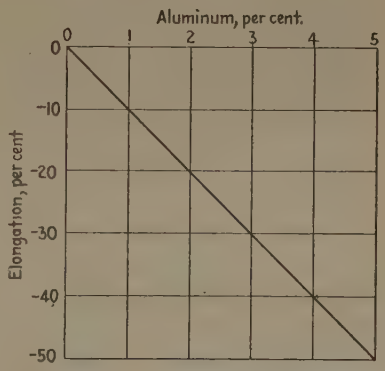

FIG. 3.—QUANTITATIVE EFFECT OF ALUMINUM ON PERCENTAGE ELONGATION OF COMPLEX BRASS.

In like manner, curves for the effects of iron and manganese have been obtained (Figs. 4, 5, 6, 7).

The question now arises as to whether the mechanical properties of a complex brass of any composition, but within reasonable limits of

56.6 per cent. copper, can be determined, given its analysis. This actually seems to be possible, as will be seen from the following discussion.

In Figs. 8 and 9 are shown the relations between the strength and the ductility of the simple brasses containing between 50 and 70 per cent. copper in the chill-cast state. Using the values on these curves as a base and employing the values quoted in Figs. 2 to 7 to determine the

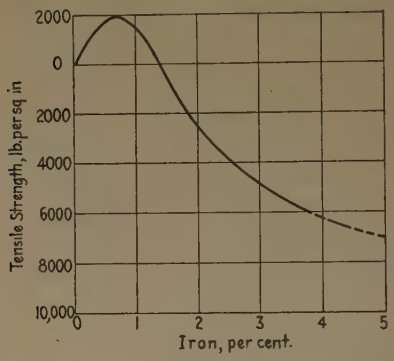

FIG. 4.—QUANTITATIVE EFFECT OF IRON ON TENSILE STRENGTH OF COMPLEX BRASS.

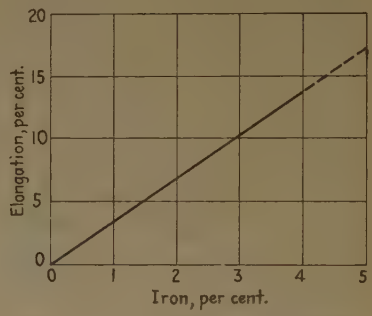

FIG. 5.—QUANTITATIVE EFFECT OF IRON ON PERCENTAGE ELONGATION OF COMPLEX BRASS.

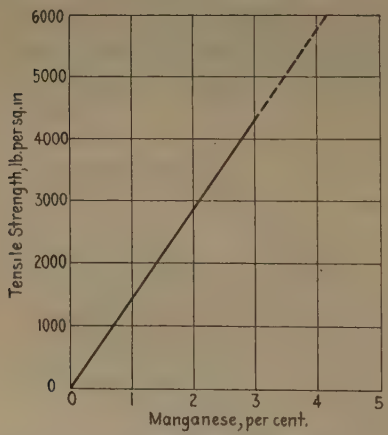

FIG. 6.—QUANTITATIVE EFFECT OF MANGANESE ON TENSILE STRENGTH OF COMPLEX BRASS.

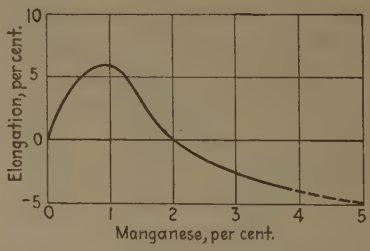

FIG. 7.—QUANTITATIVE EFFECT OF MANGANESE ON PERCENTAGE ELONGATION OF COMPLEX BRASS.

effects of aluminum, iron and manganese on this base, the mechanical properties of a very wide range of alloys appear to be capable of estimation.

As an example of the use of these curves one may take an alloy containing: copper, 51.95 per cent.; iron, 3.82 per cent.; aluminum 1.88 per cent.; manganese, 0.98 per cent.

Fig. 8 shows that the strength of a simple brass containing 51.95 per cent. copper is about 72,700 lb. per sq. in.; Fig. 4 shows that 3.82 per cent. iron reduces the strength of such a brass on the average by about 6000

lb. per sq. in.; Fig. 2 shows that 1.88 per cent. aluminum raises the strength by about 26,000 lb. per sq. in. (average) and Fig. 6 shows that 0.98 per cent. manganese increases the strength by about 1400 lb. per sq. in. (average). The estimated strength for this alloy will be:

	Lb. per Sq. In.
Strength of simple brass	72,700
Increase due to Al	26,000
Increase due to Mn	1,400
	100,100
Decrease due to Fe	−6,000
	94,100

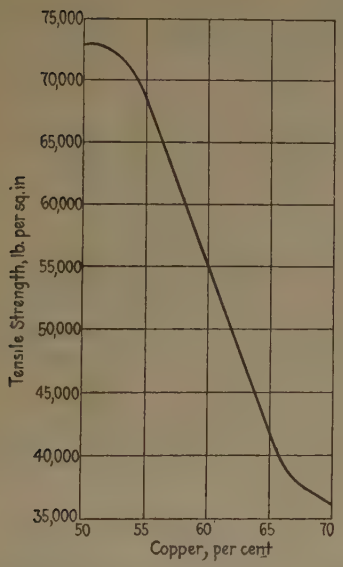

Fig. 8.—Effect of copper on tensile strength of simple brass.

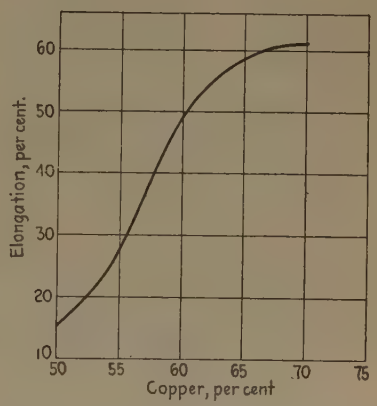

Fig. 9.—Effect of copper on percentage elongation of simple brass.

The actual strength of this alloy (chill-cast) as obtained by test was 92,200 lb. per sq. in.; *i. e.*, the estimate of strength is only 2 per cent. too high.

As to percentage elongation, following are the values:

	Per Cent. in 2 In.	
Elongation of simple brass	19	(Fig. 9)
Increase due to Fe	13	(Fig. 5)
Increase due to Mn	5	(Fig. 7)
	37	
Decrease due to Al	−20	(Fig. 3)
	17	

The actual elongation of this alloy (chill-cast) was 18.5 per cent.

Curves have also been drawn to show the relationship between the proportional limit and the tensile strength and the yield point (0.2 per cent. plastic deformation) and the tensile strength of these alloys. These are shown in Figs. 10 and 11. The scatter of the points about these curves was considerable and the estimates of proportional limit and yield point may for this reason be very inaccurate for certain alloys. Nevertheless, the curves are given for what they are worth. For the alloy just described the proportional limit (from Fig. 10) is estimated to be 26,600 lb. per sq. in. and the yield point, 41,600 lb. per sq. in. The actual values for these properties were 16,600 and 28,000 lb. per sq. in., respectively. This shows how far from correct estimates of the proportional limit and the yield point based on the curves shown in Figs. 10 and 11 may be in certain cases. It must be noted, however, that this

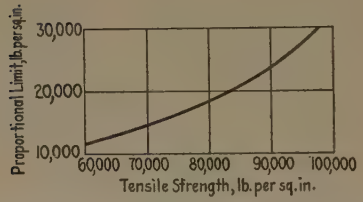

FIG. 10.—RELATIONSHIP BETWEEN PROPORTIONAL LIMIT AND TENSILE STRENGTH OF BRASS.

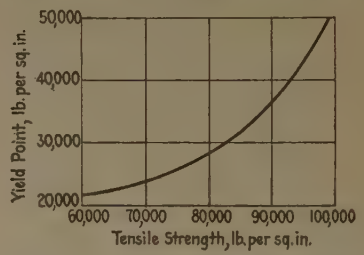

FIG. 11.—RELATIONSHIP BETWEEN YIELD POINT AND TENSILE STRENGTH OF BRASS.

is an exceptional case, as will be realized if a comparison is made between the estimated and actual values for these properties quoted in Table 5, and for which the average values are given here:

		Lb. per Sq. Lb.
Average proportional limit (for 36 alloys)	Actual	25,400
	Estimated	24,000
Average yield point (for 36 alloys)	Actual	32,000
	Estimated	29,400

Table 5 has been prepared to give some idea of the value of these curves in estimating the strength of complex brasses. This embodies (1) the results of actual tests on two series of complex brasses, including those referred to in Table 2, and (2) estimates of their properties based on the curves in Figs. 2 to 11.

Table 5 shows that, on the whole, a very close approximation to the average mechanical properties of any complex brass may be arrived at by the use of the curves. In this connection it is of interest to note that the average strength of the first group of alloys of Table 5, as tested, was 78,000 lb. per sq. in. and, as estimated, was 79,200 lb. per sq. in. The average elongation (tested) was 31.3 and (estimated) was 29.1. The difference between these two values is well within the limits of error in

TABLE 5.—*Actual (First Line) and Estimated (Second Line) Properties of Complex Brasses*

No.	Cu, Per Cent.	Mn Fe, Per Cent.	Al, Per Cent.	Mn, Per Cent.	Elect Res., Microhms per Cm. Cube	Prop. Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elong. in 2 in., Per Cent.	Red. of Area, Per Cent.
44	56.41	0.23	0.47	0.94	10.10	15,000	24,700	75,200	25.1	26.8
					10.41	16,600	26,000	76,100	36.5	
45	56.25	0.07	0.51	1.78	13.11	17,900	28,400	78,800	25.9	21.7
					13.65	16,700	26,200	76,300	30.0	
46	56.66	0.12	0.50	3.57	20.55	20,100	31,800	79,400	27.2	24.7
					20.90	17,700	27,400	78,700	26.0	
47	57.33	0.07	0.88	0.94	10.43	17,300	27,500	77,600	23.7	22.1
					10.67	17,300	26,800	77,600	35.0	
48	56.32	0.04	0.93	1.84	13.75	20,800	30,700	83,300	26.7	20.8
					14.10	19,700	29,900	82,700	26.0	
49	56.68	0.07	0.93	3.55	20.25	24,500	37,600	84,800	20.1	19.9
					21.01	20,200	31,000	84,100	22.5	
50	56.94	0.07	1.43	1.00	10.93	19,900	30,000	85,800	24.9	23.9
					11.13	21,000	32,000	85,600	28.0	
51	56.15	0.07	1.42	1.83	14.26	20,900	34,100	89,200	25.9	22.9
					14.31	23,300	35,700	89,700	26.0	
52	57.44	0.07	1.54	3.67	21.40	33,800	39,200	92,300	16.4	18.4
					21.93	23,200	35,400	89,300	21.5	
17	56.15	1.04	0.38	0.84	10.10	15,600	24,300	78,300	35.1	31.4
					10.38	16,300	26,000	75,400	37.5	
53	56.04	0.90	0.52	1.78	14.09	19,100	27,900	69,900	19.0	21.5
					14.12	18,000	27,700	79,200	26.5	
54	55.29	1.12	0.50	3.58	20.40	20,500	35,200	79,600	21.5	21.9
					21.28	20,000	30,600	83,800	24.0	
20	56.14	0.90	0.93	0.87	10.10	16,800	26,800	85,900	34.0	31.8
					10.69	20,300	31,000	84,100	32.0	
21	56.50	1.07	0.88	1.83	14.27	22,100	31,400	86,600	35.9	32.3
					14.70	19,400	29,800	82,600	30.5	
22	57.07	1.07	0.94	3.64	22.05	22,300	33,900	80,800	25.5	23.7
					22.04	20,700	31,300	84,700	28.0	
55	56.35	1.12	1.73	0.91	11.10	20,900	34,600	89,200	21.4	21.1
					11.42	19,100	29,300	81,800	26.0	
24	56.47	1.21	2.10	1.80	14.42	23,300	36,000	95,600	34.1	31.0
					15.77	21,300	32,200	85,900	19.0	
56	57.10	0.60	1.72	3.71	N.O.	27,500	51,000	97,600	19.9	18.2
						26,800	42,300	94,400	18.5	
57	56.35	2.08	0.41	1.01	11.29	10,800	22,300	71,200	38.2	36.2
					11.74	14,800	24,200	71,000	43.0	

TABLE 5.—(*Continued*)

No.	Cu, Per Cent.	Fe, Per Cent.	Al, Per Cent.	Mn, Per Cent.	Elect. Res., Microhms per Cm Cube	Prop. Limit, Lb. per Sq. In.	Yield, Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elong. in 2 in., Per Cent.	Red. of Area, Per Cent
27	57.27	1.43	0.53	1.73	14.60 14.46	15,300 15,500	23,800 25,000	71,400 73,300	46.0 39.5	38.5
59	57.19	2.11	0.41	3.83	23.37 23.19	17,500 15,300	24,000 24,800	65,300 72,500	26.7 37.0	25.7
60	57.00	2.11	0.91	0.96	11.45 11.93	16,000 16,600	26,900 26,000	78,500 76,000	40.2 40.0	41.8
61	56.90	1.78	0.86	1.91	15.27 15.51	16,800 17,400	30,300 27,000	75,500 78,000	22.7 33.5	24.1
62	56.73	1.84	0.94	3.76	23.05 22.91	18,800 19,000	35,100 29,000	83,200 81,400	27.7 28.5	26.0
63	56.30	1.84	1.77	0.99	11.45 12.20	21,000 23,000	30,500 35,000	93,900 88,900	28.6 27.0	28.2
64	57.11	2.06	1.89	1.90	14.91 16.10	26,500 23,300	43,500 35,400	95,500 89,200	24.5 25.5	24.5
65	56.52	1.86	1.84	3.81	20.40 23.58	30,700 25,600	50,700 39,200	95,200 92,600	16.1 26.0	17.6
35	57.05	3.80	0.51	0.99	12.28 12.86	14,300 13,700	22,200 23,000	66,800 66,900	54.3 51.0	49.7
36	56.74	3.51	0.54	1.69	N.O.	12,500 14,300	23,500 23,800	67,500 69,400	35.0 42.5	32.1
37	56.64	3.87	0.61	3.53	N.O.	15,000 15,400	30,000 25,000	70,300 72,900	48.0 37.5	40.7
38	57.52	4.12	0.91	1.01	12.78	14,900 14,800	24,300 24,300	70,300 71,100	48.2 50.0	42.8
39	56.72	3.90	0.95	1.77	15.60 16.19	14,600 16,300	26,100 25,700	73,900 75,100	47.4 39.5	41.4
40	58.36	4.01	1.01	3.67	22.31 24.16	15,600 11,700	25,900 21,500	69,100 60,100	40.7 41.0	35.3
41	56.76	3.93	1.41	0.97	N.O.	17,500 18,100	33,200 28,000	88,500 79,700	N.O. 40.5	19.2
68	56.27	4.45	1.94	2.01	16.25 17.91	24,100 22,100	45,300 33,700	86,400 87,500	11.6 29.5	15.1
69	56.05	3.87	1.82	3.80	20.81 25.02	23,600 23,700	50,300 36,300	99,500 90,300	21.1 23.0	33.1
ALLOYS NOT USED AS A BASIS IN THE PREPARATION OF THE CURVES, ETC.										
18	57.14	0.11	0.41	1.84	13.27 14.00	14,900 15,500	27,100 25,000	76,300 73,100	27.2 34.0	24.9

TABLE 5.—(*Continued*)

No.	Cu, Per Cent.	Fe, Per Cent.	Al, Per Cent.	Mn, Per Cent.	Elect. Res., Microhms per Cm. Cube	Prop. Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elong. in 2 in., Per Cent.	Red. of Area, Per Cent.
19	57.83	0.13	0.47	3.67	21.20	15,900	25,200	72,100	37.7	32.4
					21.48	15,700	25,200	73,800	31.5	
25	56.85	0.46	1.41	3.70	21.63	29,700	39,000	98,500	27.6	24.6
					22.15	24,300	37,000	90,800	19.5	
26	57.01	0.31	0.48	0.92	10.43	14,500	22,600	73,400	36.1	29.4
					10.48	15,000	24,300	71,500	39.0	
28	57.07	1.25	0.50	3.63	22.39	20,500	27,500	73,500	38.5	35.9
					21.87	17,300	27,800	77,500	32.5	
29	56.67	1.07	0.98	0.91	10.78	16,300	27,200	75,600	20.5	20.7
					10.18	19,400	29,700	82,300	34.5	
30	56.88	1.64	0.94	1.79	14.59	19,300	29,200	80,100	30.9	26.1
					14.97	18,300	28,200	80,200	33.5	
31	57.05	0.98	0.92	3.64	N.O.	22,500	31,700	83,500	40.0	35.0
						20,800	31,700	85,100	27.5	
32	56.95	1.91	1.53	0.91	11.10	21,600	34,300	92,800	31.1	27.5
					11.92	20,100	30,800	83,900	33.5	
33	56.71	2.03	1.37	1.78	14.77	25,800	37,500	96,100	31.7	29.6
					15.35	20,300	31,000	84,200	35.0	
34	57.45	0.84	1.24	3.70	21.72	32,900	45,300	98,400	33.3	26.9
					22.36	19,300	29,300	82,000	26.5	
42	57.18	3.98	1.30	1.81	15.08	22,600	35,500	83,900	21.3	23.4
					16.69	17,700	27,300	78,400	38.5	
43	57.16	4.20	0.95	3.30	22.88	16,500	26,300	72,000	48.7	43.4
					23.03	16,700	26,200	76,300	38.5	
58	59.83	2.25	0.42	1.93	16.91	13,100	22,500	61,500	38.3	45.2
					15.96	12,800	22,300	64,200	52.0	
66	55.80	4.53	0.63	1.94	16.08	11,400	24,200	63,300	19.4	22.9
					16.98	15,300	24,700	72,300	42.0	

testing. For the other group of tests shown in Table 5 the following values were obtained:

	As Tested	As Estimated
Strength	80,100	78,500
Elongation	32.2	34.5

It is concluded then that the curves given in Figs. 2 to 11 may be used as the basis of estimating the average mechanical properties of any chill-cast complex brass containing aluminum, manganese and iron and from about 50 to about 60 per cent. of copper.

Turning now to the effect of tin on complex brass, it is certain that this element increases the strength of brass. In all probability, were its effect on the ductility of brass not so deleterious when it is present in proportions of more than from ¾ to 1.5 per cent., the relation between strength and tin content could be represented by a curve like that in Fig. 12 and that between elongation and tin content by the curve in Fig. 13. Using this curve as the basis of calculating the effect of tin, estimates (Table 6) of the strength of certain of the alloys referred to in Table 2 have been made.

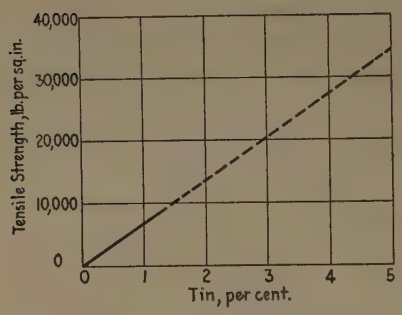

FIG. 12.—APPROXIMATE QUANTITATIVE EFFECT OF TIN ON TENSILE STRENGTH OF COMPLEX BRASS.

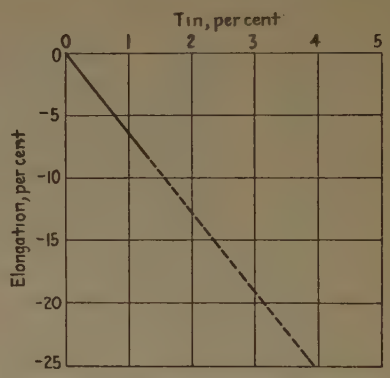

FIG. 13.—APPROXIMATE QUANTITATIVE EFFECT OF TIN ON PERCENTAGE ELONGATION OF COMPLEX BRASS.

TABLE 6.—*Estimates of Strength of Certain Alloys*

	Cu Per Cent.	Fe Per Cent.	Al Per Cent.	Mn Per Cent.	Sn Per Cent.	Prop. Limit Lb. per Sq. In.	Yield Point Lb. per Sq. In.	Tensile Str. Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Red. of Area, Per Cent.	Remarks
8	56.81	0.34	1.12	0.74	0.48	21,000	34,200	84,800	21.5	21.7	Actual
						21,400	32,300	86,000	28.0		Estimated
13	56.96	0.17	0.49	1.56	0.36	20,000	34,500	81,900	21.0	22.1	Actual
						17,000	26,500	76,700	32.0		Estimated
17	57.12	0.79	0.99	0.76	1.56	28,000	48,000	94,400	22.3	23.4	Actual
						25,000	38,300	91,800	15.0		Estimated
21	56.90	0.95	0.95	1.50	1.60	30,000	52,600	92,500	14.0	14.5	Actual
						26,000	40,000	93,000	22.5		Estimated

The agreement here between the estimated and the actual values is not quite so good, but, even so, the limits of experimental error are by no means grossly exceeded.

The effect of nickel on brass has been the subject of considerable inquiry. A review of many tests by various workers makes it possible to present Fig. 14 as representing approximately the effect of this element on the strength of brass. Nickel lowers the strength of brass when it

replaces zinc; it increases the ductility slightly, if at all, at first; *i. e.*, up to about 1 per cent. In quantities of more than 1 per cent. nickel improves the ductility of the alloys under discussion, but apparently not to the same extent as does iron. No curve is drawn for the effect of nickel on the ductility of brass as the results available for consideration were so discrepant.

As showing the use of Fig. 14 in conjunction with the other curves, the results in Table 7 are of interest. The tests recorded are due to Smalley.[33] On the whole, the estimated strengths are good, though the first test results and the last two are widely divergent from the estimated values.

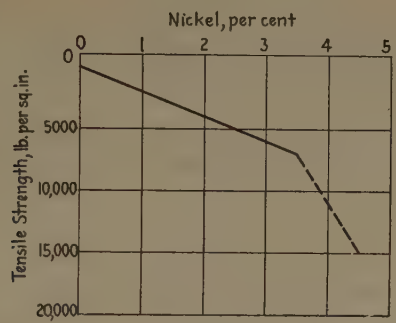

FIG. 14.—APPROXIMATE QUANTITATIVE EFFECT OF NICKEL ON TENSILE STRENGTH OF COMPLEX BRASS.

The effect of nickel needs further investigation, though at the moment it does not appear that this element can be of much service as far as its effect on the mechanical properties of these alloys are concerned. It may possibly improve the casting qualities of the alloys, but here the question of the cost of the metal relative to, say, iron, which is also supposed to improve the casting qualities of these alloys, should be considered.

As to the electrical properties of these alloys, it appears that aluminum is almost without influence on the resistivity of brass, at most increasing it by not more than 0.5 microhms per cu. cm. per cent. of the metal substituted for zinc. Iron is somewhat more potent, increasing the resistivity by about 0.6 microhms per cu. cm. per cent. Manganese is extremely powerful, raising the resistivity by as much as 4 microhms per cu. cm. per cent. under these conditions.

In conclusion, it is interesting to note the agreement between the mechanical properties as estimated by the author and as determined by Smalley[33] on a series of complex brasses of the type referred to in this paper (see Table 8).

A study of the author's work leads to the view that the effects of the elements aluminum, iron, manganese, and tin upon the mechanical properties of brass containing in the neighborhood of 56.5 per cent. copper (possibly from 50 to 60 per cent.) are cumulative. Hence, given

TABLE 7

Cu, Per Cent.	Ni, Per Cent.	Al, Per Cent.	Fe, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Red. of Area, Per Cent.	Remarks
56.68	0.92			47,300	23.0	36.4	Actual
				57,000			Estimated
59.00	1.90			53,200	56.0	49.7	Actual
				54,000			Estimated
59.02	4.03			41,000			Actual
				42,200			Estimated
58.88	3.08	1.43	0.10	69,000	34.0	35.5	Actual
				73,000			Estimated
55.60	3.27	1.64	0.11	77,500	15.0	18.3	Actual
				83,500			Estimated
60.50	2.96	2.89		82,300	19.0	21.5	Actual
				81,900			Estimated
69.42	3.77	4.93	0.10	76,000	13.0	18.3	Actual
				69,200			Estimated
58.95	3.13	3.95	0.40	95,300	6.0	8.4	Actual
				93,300			Estimated
60.02	3.00	4.10	1.45	99,800	12.0	15.0	Actual
				90,000			Estimated
			Sn				
59.06	2.83	3.28	0.75	83,000	4.5	8.4	Actual
				93,200			Estimated

the analysis of a complex brass and knowing the mechanical properties of the basic alloy and the effects of the elements present in the alloy, other than copper and zinc, the mechanical properties of the mixture in the chill-cast state can be estimated. In what proportions the effects of these elements would be reflected in a complex brass in the sand-cast state it is impossible to say. There seems to be no reason, however, why these elements should not behave in the same order, if not to the same degree, in alloys in both the chill-cast and the sand-cast conditions. Assuming this to be the case, the author's work provides a logical basis for the determination of the alloys best suited for use as complex brasses.

It seems likely that the use of metals other than aluminum, iron, and manganese in these complex brasses is quite unwarranted, mainly because those which might be used are of greater cost than those now generally employed. It is doubtful, however, whether manganese could be reason-

TABLE 8.—*Complex Brasses (Chill-cast) Tested by Smalley*

No.	Cu, Per Cent.	Fe, Per Cent.	Al, Per Cent.	Mn, Per Cent.	P, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
AM-2.....	59.45	0.40	1.56	1.97	0.02	80,400	22.0
						83,200	33.0
AM-4.....	58.15	0.25	2.24	4.10	0.08	90,700	14.0
						95,800	16.5
AM-5.....	59.45	0.22	0.98	3.49	0.01	71,200	25.0
						78,100	34.5
AM-6.....	58.74	0.10	3.12	3.92		80,400	13.0
						83,900	7.0
AM-11.....	58.76	0.20	1.95	3.43		88,700	13.0
						89,700	21.5
AM-12.....	58.87	0.10	2.94	0.96		86,600	11.0
						94,800	27.5
AM-13.....	58.32	0.10	3.12	3.92		101,500	13.0
						101,200	7.0
AM-14.....	58.11	1.65	1.95	3.98		95,000	14.0
						91,100	24.0
AM-23.....	57.23	0.20	2.59	2.08		92,700	12.0
						98,000	18.0
AM-3C.....	59.34	0.20	3.10	2.02		96,200	15.0
						95,900	16.0
AM-3D.....	57.07	0.32	3.12	1.81		98,200	20.0
						102,200	8.0
1-F.....	58.96					55,800	45.0
						58,000	45.0
1-F-1.....	59.37	0.95				60,000	44.0
						58,600	50.0
1-F-3.....	59.12	2.52				59,300	46.0
						52,800	54.5
2-F.....	53.41					66,500	24.0
						71,400	23.0
2-F-1.....	51.72	1.05				69,200	16.0
						74,200	22.5
2-F-2.....	50.77	2.20				74,000	17.0
						69,700	21.5

ably eliminated, in view of its marked effect on ductility when present in small proportions (see Fig. 7). This effect must be of some importance, since the increase in ductility is coincident with a definite increase in strength. There is no clear evidence to show that the presence of manganese is objectionable on account of its effect on the casting properties of these alloys provided they contain aluminum, hence the elimination of manganese on these grounds can scarcely be entertained.

If we accept the view that all three elements—aluminum, iron, and manganese—are of real value in these complex alloys, it seems logical to consider the high-strength brasses as aluminum brasses to which small proportions of iron and manganese are added, the former for the purpose of increasing the ductility without reducing the strength (see Figs. 4 and 5), the latter for the purpose of increasing the strength without reducing the ductility (see Figs. 6 and 7).

Acknowledgment

The author wishes to express his appreciation of the help afforded him by J. Gier, of the Research Department of the Westinghouse Elec. & Mfg. Co., in preparing these alloys, and by T. F. Hengstenberg, of the same department, in testing them. His thanks are also due to the Westinghouse Elec. & Mfg. Co. for permitting the results recorded in this paper to be published.

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DISCUSSION

P. E. McKinney, Washington, D. C. (written discussion).—This report on the effect of hardening and strengthening elements in the high-strength brasses covers a field of research in non-ferrous metallurgy that has been inadequately covered in the past and the author's efforts in this direction are sure to offer a valuable contribution to our knowledge on this subject.

In considering the various combinations of hardening elements the author has based his study on materials in which there is maintained a more or less constant percentage of copper leaving the zinc as a variable difference between the sum of a constant copper content plus the varying content of the hardeners, aluminum, iron, manganese and tin. This presents for consideration a number of alloys which are metallurgically improperly balanced and not compounded in such ratios as to produce the full effect of the hardeners. It also precludes from consideration a large number of practicable combinations which have considerable industrial value.

The last paragraph in the author's paper, which contends that these materials are actually aluminum brasses, is fully concurred in. Practically all of the so-called manganese bronzes are in reality aluminum brasses to which the hardeners, iron and manganese, are added. It is now rather generally recognized that brasses containing high percentages of iron and manganese but strictly free from aluminum are quite unreliable. While under ideal conditions considerable percentages of iron and manganese can be added to aluminum-free brass, this is not commercially practicable nor are the alloys reliable on account of the tendency to segregation when aluminum is absent.

Since these alloys are fundamentally aluminum brasses it is believed that the combinations of copper, zinc and aluminum should be given first consideration. Considering the straight aluminum brass, we can safely use as a basic alloy the combination copper 58 per cent., zinc 42 per cent. The strength of this straight copper-zinc alloy can be increased without serious effect on ductility by adding aluminum and reducing zinc. Experience has shown that in order to obtain this increase of strength without serious detriment to ductility it is necessary to reduce the zinc content of the alloy by approximately three times the amount of aluminum additions. With the basic 58:42 brass this results in a progressive decrease in zinc content and increase in copper content with increasing additions of aluminum to the alloy. This general rule holds true with aluminum additions at least up to about 6 per cent.

The copper-zinc alloys, while showing high strength, are sadly lacking in elasticity and hardness and require additions of hardening and stiffening agents such as iron or manganese to make them useful for structural purposes. In addition to the strengthening effect of aluminum in these alloys this element serves a very important function in rendering the hardeners, iron and manganese and particularly the former, fully soluble in the brass. It is believed that this tendency to increase solubility, particularly of iron, is due to the fact that aluminum reduces all oxides of iron that are introduced into the alloy and tends to overcome the well-known tendency of iron to improperly combine with copper. In this respect aluminum acts with considerably greater efficiency than zinc. Experience has shown that in order to get the maximum hardening and stiffening effects of the iron and manganese it is necessary to have present in the alloy a percentage of aluminum representing at least 50 per cent. of the iron and manganese additions. This ratio of combination is particularly important where the iron is used as a predominating hardening element. It appears that iron is somewhat more recalcitrant to perfect amalgamation with the alloy in the absence of aluminum than in manganese. It is believed that the difficulties of adding iron to the alloy in the absence of an ample amount of aluminum has been one of the principal reasons why manganese is preferred by many metallurgists over iron. In the writer's opinion iron alone will serve as a very efficient hardener if it is possible to combine in the particular alloy sufficient aluminum to care for the proper combination of the elements. In actual manufacturing of these alloys it is usually, however, considered good psychological practice to add some manganese as a hardening agent, because the trade as a whole seems to recognize that manganese is necessary in such alloys, although there is no definite information which would confirm this belief.

With the proper combination of iron and manganese in these aluminum brasses it is not at all uncommon to have material that is capable of showing a true elastic limit as high as 30,000 lb. per sq. in. with yield point running from 45,000 to 50,000 lb. per sq. in. These unusually high values are only possible where alloying elements, zinc, aluminum, iron and manganese, are properly balanced. In a properly balanced high-strength brass the copper can be considered simply as inert diluting agent, present principally in the form of solid solution. It is believed that the strengthening combinations in these brasses are dependent more on the combination of zinc, iron and manganese than on copper and that in practically all cases the copper plays no significant part in the alloy other than as a matrix metal.

The author's statements to the effect that tin is apparently an unnecessary constituent in these alloys is fully concurred in. While originally tin was considered a necessary constituent, it has been definitely established that the hardening effect of tin is never attended with the same maintenance of initial ductility in this alloy as can be accomplished with iron or manganese at considerably less cost. While many present-day alloys contain some percentages of tin, this exists mostly as contamination from scrap material used. It would be considered unwise practice to deliberately add metallic tin to this alloy. Existing specifications for manganese bronze permit tin up to 1.50 per cent. but do not require any minimum percentage.

In making up these alloys, the author says that the copper was melted first, then the iron was added, followed by manganese. This method of combining these brasses is considered improper melt practice and probably accounts for some of the individual test records that show low ductility.

The practice of adding metallic iron to the molten copper, especially without previous deoxidation of the copper, would tend to introduce some oxide of iron into the alloy, on account of the deoxidizing effect of iron on copper oxide. The resultant iron oxide will not readily free itself from molten copper and while it is possible to eliminate some of these oxides by the later additions of manganese, aluminum and zinc, it is not believed that the elimination of all of these oxides can be invariably

accomplished. In the writer's opinion, it is far safer when alloying these brasses from virgin metals to melt copper first, to be followed by the aluminum and manganese, then iron and zinc. The iron will dissolve far more readily in the copper-aluminum alloy than in the straight copper. It is believed that many cases of hard spots reported in high-strength brass are due to improper melting practice which permits the retention of iron oxide.

It is suggested that the excellent work covered in this paper be supplemented by a further study of alloys in which zinc is considered as the principal ingredient for study in combination with aluminum, manganese and iron as strengthening, stiffening and hardening agents and copper as the variable factor. This investigation, which would go into the field of alloys containing as high as 70 to 75 per cent. copper, would add considerable additional data to the very valuable information contained in this paper.

L. H. Fawcett, Washington, D. C. (written discussion).—In actual foundry production, casting in sand and using scrap metal, it is more difficult to maintain high physical values than is possible in a metallurgical laboratory. Metal poured in sand cools slowly, which allows time for liquidation. The use of scrap makes it more difficult to maintain a definite composition.

We made 22 consecutive manganese-bronze (Mn brass) melts (7000 lb. each) of the following average chemical analysis: Cu, 58.25; Zn, 39.00; Al, 0.80; Mn, 0.70; Fe, 1.00; Sn, 0.25 per cent. The physical properties obtained as cast in sand are as follows:

	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
Average	76,747	26.4
Highest	82,000	25.8
Lowest	71,800	36.3

These melts were compounded with used small arms cartridge cases and manganese-bronze scrap resulting from previous melts, to which were added the necessary amounts of slab zinc, scrap aluminum, metallic manganese and sand-blasted boiler-plate scrap.

Another manganese-bronze combination which the author does not mention is obtained by reducing the zinc content and raising the percentage of the other ingredients: *i. e.*, Cu, 70.80; Zn, 16.35; Al, 6.16; Mn, 4.39; Fe, 2.30 per cent. Results of a melt of this composition obtained in foundry production is given below:

	Proportional Limit, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.
Sand cast	22,900	91,200	28.3	32.8
Chill cast	30,600	97,000	23.3	25.7

M. G. Corson, New York, N. Y.—It is not necessary to ascribe the influence of aluminum to the element itself. The proportionality of the influence could be obtained also if the aluminum should form some kind of a compound strengthening the alloy by dispersion hardening. In fact, if we consider the figures of aluminum and manganese, we will find that manganese itself increases the electrical resistivity, but as soon as sufficient aluminum is added the resistivity drops, and the best conductivity seems to be obtainable when the ratio of manganese to aluminum is about two to one, corresponding to the compound MnAl.

Moreover, I do not believe that an addition of 1 per cent. of any element remaining in solid solution would increase the ultimate strength of a given brass by as much as 25 per cent. There is not a chance for a hardening of this order to result from the formation of a solid solution. If for instance, aluminum were added to a pure beta brass the hardening, if any occurred, would most probably be due to the formation of a delta aluminum bronze dispersed in the beta brass. With manganese present, there is far more chance for these two elements to form MnAl and the resistivity figures given by Mr. Ellis corroborate this suggestion of mine.

It is frequently said: Let's keep the copper at a fixed percentage and substitute some aluminum or something else for the equal amount of zinc. I believe that this expression is entirely incorrect. One cannot substitute one metal for another in alloys, particularly in a solid solution. What we can do is to take a certain base alloy and dilute it with some other element. So in the case of a ternary brass one would have to use the triangular of a diagram and to draw a line from the summit of the third metal, say, tin or aluminum, to the representative point of the base alloy upon the base of the triangle (Fig. 15).

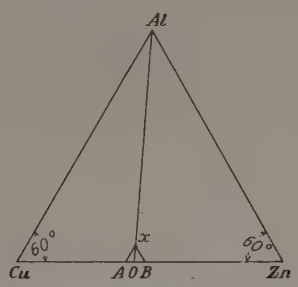

FIG. 15.—AN ALLOY *X* DOES NOT REPRESENT THE ALLOY A WHERE PART OF THE COPPER HAS BEEN REPLACED BY AL, NOR DOES IT REPRESENT ALLOY B WITH PART OF THE ZINC REPLACED BY AL, BUT THE ALLOY O DILUTED WITH AL.

F. H. CLARK, New York, N. Y.—Has Mr. Ellis studied the microstructure of these 60:40 brasses and noted the effect of a small addition of iron, aluminum or manganese on the transition point which occurs at 470° C.?

O. W. ELLIS (written discussion).—Mr. McKinney's discussion of this paper deserves most careful attention. The author fully appreciates his criticism of the narrowness of the field covered by the experiments. It is true that a series of tests on alloys containing higher percentages of copper are necessary, if there are to be included those "metallurgically balanced" mixtures which are finding their place in engineering service today. However, a start must be made somewhere and it was decided to begin with the alloys having a copper content approaching that of the well-known Parson's manganese bronze. Whether similar series of tests can be made on alloys of higher copper content by the author he cannot at the moment say; it is, however, a fascinating field for investigation.

The author is glad to have confirmation of his contention that these alloys are essentially aluminum brasses to which iron and manganese are added for the purpose of obtaining specific properties. While this view has doubtless been held by many workers in this field, the author has never seen or heard the view expressed. That a fuller investigation of the effect of aluminum on brass is deserved goes almost without saying.

Mr. McKinney's remarks with regard to the method of melting are well taken, if we are considering what might be termed ordinary foundry practice. It is true

that we melted the copper and then introduced the iron, but the melting was done in an induction furnace in graphite crucibles, and the possibility of oxidation of the copper during melting was extremely remote. The iron, after it had been introduced, was allowed to remain in the copper until there was absolutely no evidence of its presence. Those who have attempted to add iron to copper under such conditions will know that as long as any undissolved iron is present it can be seen as clearly and definitely as one could wish. It was not until we were absolutely satisfied that the iron had completely disappeared by solution in the copper that we proceeded with our experiment.

Only once did we have the least evidence of trouble in this connection, and that was in about the third melt, which, of course, was rejected. In that case some undissolved iron had remained in the melt and this rose to the top of the ingot when we poured.

Mr. Fawcett's remarks regarding the mechanical properties of certain sand-cast alloys are interesting. They have raised a point in my mind in regard to the relationship between the mechanical properties of chill-cast and sand-cast alloys. I may be too hastily jumping at conclusions here, but an examination of a large number of tests has led me to believe that the difference between the mechanical properties of sand-cast and chill-cast alloys is greater in the case of low-strength alloys than in the case of high-strength alloys. In other words, one might expect that the estimated mechanical properties obtained from the curves shown in the paper would more closely correspond with the properties of sand castings the more complex, if you like to call it, the alloy. This point, however, deserves further investigation.

Mr. Corson's remarks are interesting. He and I have discussed the possibility of the formation of an intermetallic compound in these alloys before. There is one thing, however, that should be mentioned here. The effect of manganese on the electrical resistivity of these alloys is uniformly the same even when the content of manganese is increased to as much as 18 per cent. Westinghouse Electric & Manufacturing Co. employs an alloy of high electrical resistivity which is essentially a brass containing a high proportion of manganese. By assuming that the effect of manganese is uniformly the same no matter what the amount present in the alloy (4 microhms per cm. cubed per cent. of manganese) I obtained a value for the resistivity of the alloy which corresponded very closely to that determined by experiments. It is difficult for me to believe that the hardness of these alloys is due to the dispersion of any constituents unless it be the iron compound of which we still have to determine the composition. Actually, the author has endeavored to treat these alloys with a view to getting the compound to go into solution and causing it to precipitate in finely divided form. So far his experiments have not been successful. This line of investigation may be worth following, however.

With regard to Miss Clark's question as to the microstructure of these alloys, we did investigate these; chiefly, however, with the view of determining the manner in which the iron constituent was distributed, because, of course, the distribution of the iron constituent in these alloys might have an extremely important effect on the mechanical properties. We found that in all cases the distribution was sufficiently uniform to enable us to say that the mechanical test results were not affected by this important factor. We have samples of these alloys remaining and it is our intention, when time permits, to follow up the investigation with micrographic and thermal work.

Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys Containing Nickel and Silicon

By W. C. Ellis* and Earle E. Schumacher,* New York, N. Y.

(New York Meeting, February, 1929)

Nonferrous alloys upon which desirable properties can be conferred by heat treatment are becoming of increasing industrial importance. The alloys of copper with a constituent which has a solubility varying with temperature are materials of this character. Some of the constituents which are effective in producing a change in the mechanical properties of these alloys upon heat treatment are, according to Corson,[1] nickel and silicon, iron and silicon, cobalt and silicon, and chromium and silicon. In addition to these elements, Gregg[2] states that the combination of beryllium and silicon is effective in producing age-hardening characteristics in copper. The effect of these elements, however, as dispersion-hardening constituents in the copper alpha solid solutions does not seem to have been studied in any considerable detail. This paper deals with the heat treatment and properties of three alpha brasses containing 3 per cent. of nickel plus silicon in the proportion necessary to form the compound nickel silicide, Ni_2Si. Some information of a preliminary nature in regard to the hardening by heat treatment of phosphor bronze containing the same percentages of nickel and silicon is included.

The method of hardening the alloys, which is effective in increasing the tensile strength and proportional limit, is similar to that used in the case of duralumin type aluminum alloys. It consists of a quench from a temperature at which the hardening constituent is in solid solution, followed by an aging at a lower temperature to precipitate the dissolved constituent in a dispersed condition. This results in an increased resistance of the alloy to deformation with an attendant improvement in the tensile properties.

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* Bell Telephone Laboratories.

[1] M. G. Corson: Copper Alloy Systems with Variable Alpha Range and Their Use in the Hardening of Copper. *Proc.* Inst. Metals Div., A. I. M. E. (1927) 435.

[2] J. L. Gregg: Dispersion Hardening in Copper-base and Silver-base Alloys. See page 409.

Preparation of Alloys

The alloys were melted under charcoal in a graphite crucible. The component metals were electrolytic copper, electrolytic nickel and commercial silicon. The zinc used in preparing the brass alloys for the preliminary study was a brass special containing 99 per cent. zinc. The zinc added to alloys Nos. 33, 34 and 35, on which final tensile tests were made, was Anaconda high grade electrolytic. Straits tin containing 99.9 per cent. tin was used in preparing the phosphor-bronze alloys. In conformity with good practice, the zinc was added to the brass alloys just prior to pouring.

The metal was cast into plates 0.75 in. thick, 4 in. wide, and 10 in. long. The plates were cold-rolled to 18 and 24 B. & S. gage sheet. Frequent annealings were necessary. The anneal consisted of heating for 15 min. at 700° C. An attempt was made to hot-roll some of the brass alloys but the plates invariably cracked in the first pass. The studies, however, did not extend over a sufficiently wide range of temperatures and reductions to permit definite conclusions to be drawn as to the hot-working qualities of these compositions.

Heat Treatment and Mechanical Properties of Nickel-silicon Brass

Effect of Heat Treatment on Hardness of Cast Alloys.—In a study of the properties of the cast alloys, it was found that the hardness could be varied through wide ranges by suitable heat treatment. The Rockwell hardness values of several of these alloys, chill-cast, quenched, and quenched and aged, are given in Table 1. The hardness in the chill-cast condition increased with the percentage of zinc in the alloy. In the compositions containing 10 and 20 per cent. of zinc the heat treatment resulted in an appreciable increase in hardness. The hardness of the alloy containing 30 per cent. of zinc was not much changed from the as-cast condition by quenching and aging. Reference to the results in a later section of this paper obtained on rolled sections would indicate,

Table 1.—*Effect of Heat Treatment on Hardness of Some Cast Nickel-silicon Brasses*

Nominal Composition			Rockwell Hardness, "B" Scale, 100-kg. Load		
Cu, Per Cent.	Zn, Per Cent.	Ni_2Si, Per Cent.	Chill Cast	Quenched from 875° C.	Quenched from 875° C., Aged 1 Hr. at 550° C.
97	0	3		−10	83
87	10	3	35	0	79
77	20	3	65	8	75
67	30	3	70	28	72

however, that considerably higher hardness values might be expected in these cast alloys from a lower aging temperature. The results do show that alloys of this composition may have possibilities in the manufacture of high-strength brass castings.

Effect of Heat Treatment on Mechanical Properties of Rolled Alloys.—An extensive study was made of the effect of heat treatment on the tensile properties of 0.040-in. sheet nickel-silicon brass containing 3 per cent. of nickel plus silicon with 10, 20 and 30 per cent. of zinc. The tensile tests were made in conformity with the best practice for sheet brass as outlined by Van Deusen, Shaw and Davis.[3]

The alloys before heat treatment were finished hard. The mechanical properties in this condition are given in Table 2.

TABLE 2.—*Mechanical Properties of Rolled Nickel-silicon Brass* 0.040 *in. Sheet; Finished Hard*

Material No.	Composition			Rockwell Hardness, "B" Scale, 100-kg. Load	Proportional Limit, Lb per sq. in.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Modulus of Elasticity, Lb. per Sq. In. $\times 10^{-6}$
	Zn, Per Cent.	Ni, Per Cent.	Si, Per Cent.					
6	9.79	2.10	0.45	98	31,000	108,000	1.0	15.7
9	19.58	2.54	0.68	93	31,000	94,800	5.0	15.2
35	30.12	2.36	0.66	98	48,000	114,000	2.5	14.0

To determine the optimum conditions of heat treatment necessary for developing the best combination of physical properties in these alloys, the one containing 10 per cent. of zinc was studied in detail. The effect on the properties of the alloy of varying each of the three following conditions, independently, was determined: (1) the quenching temperature, (2) the quenching temperature with subsequent aging at constant temperature, (3) the aging temperature after quenching from a given temperature. The information obtained with this one alloy made it unnecessary to carry out an equally detailed investigation in the determination of the best heat treatments for the alloys of higher zinc content. Accordingly, only the effect of aging at several temperatures after quenching from two temperatures was studied in the case of alloys containing 20 and 30 per cent. of zinc.

The change in the mechanical properties of the alloy containing 10 per cent. of zinc resulting from a variation of the quenching temperature is shown in Fig. 1. The specimens were held at the temperature of quenching for 15 min. The hardness of the alloy decreases as the temperature of quench is raised to 800° C. Quenching from 900° C. results in properties almost the same as those obtained by quenching from

[3] H. N. Van Deusen, L. I. Shaw and C. H. Davis: Physical Properties and Methods of Test for Sheet Brass. *Proc.* Am. Soc. Test. Mats. (1927) **27**, Pt. 2, 173.

800° C. This indicates that the nickel and silicon are completely in solution at 800° C., and that no material benefit to the properties may be expected from quenching at a higher temperature. . Moreover, the drastic quench from 900° C. has a tendency to crack the thin sections of metal.

From Fig. 2, which shows the mechanical properties of this material quenched at temperatures from 700° to 900° C., followed by aging for

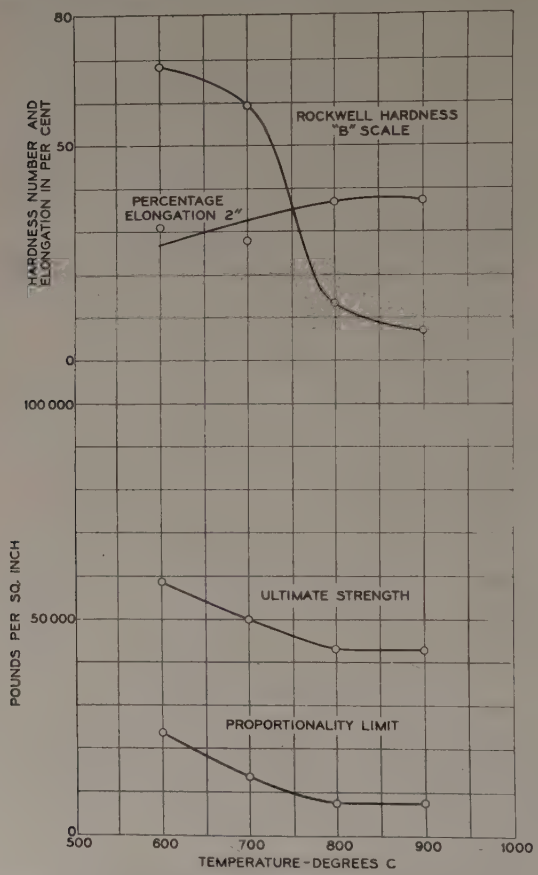

FIG. 1.—EFFECT OF QUENCHING TEMPERATURE ON MECHANICAL PROPERTIES OF NICKEL-SILICON BRASS CONTAINING 9.79 PER CENT. ZN, 2.10 PER CENT. NI AND 0.45 PER CENT. SI.

1 hr. at 500° C., it is evident that raising the quenching temperature considerably above 800° C. results in somewhat inferior properties in the heat-treated material. This may be due to the ordinary type of deterioration observed in brass annealed at unduly high temperatures. This class of alloys, however, when quenched from 800° to 850° C. seems to be free from this objection. As a result of these considerations, it seems probable that the best quenching temperature is 800° C.

It remains to determine the best aging temperature. Fig. 3 shows the results obtained on aging this alloy, after quenching from 800° C., at temperatures from 300° to 600° C. The best mechanical properties resulted from an aging treatment at 500° C. for 1 hr. Aging for 1 hr. at 600° C. caused an appreciable softening of the alloy accompanied by a decrease in strength.

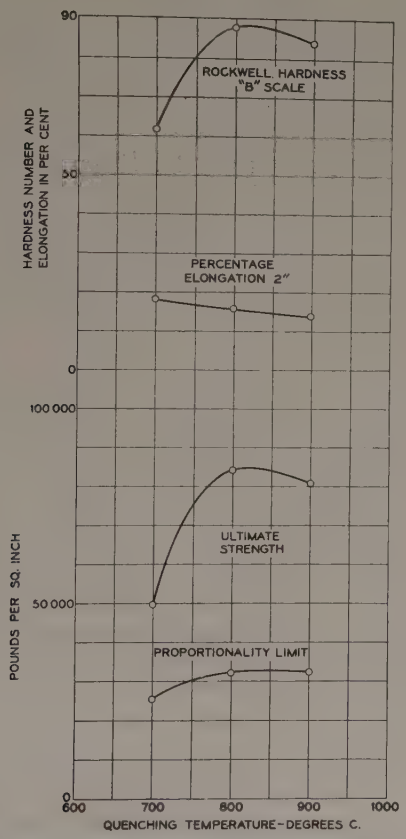

FIG. 2.—EFFECT OF QUENCHING TEMPERATURE ON MECHANICAL PROPERTIES OF HEAT-TREATED NICKEL-SILICON BRASS, CONTAINING 9.79 PER CENT. ZN, 2.10 PER CENT. NI AND 0.45 PER CENT. SI. SPECIMENS WERE AGED FOR 1 HR. AT 500° C.

To determine whether 1 hr. was too long a time for the aging at 500° C., one specimen was aged for 10 min. The hardness number and ultimate strength for this specimen, as shown in Table 3, were sufficiently high to indicate that the major portion of precipitation had occurred in 10 min. Subsequent tests showed that the Rockwell hardness numbers, in the case of this alloy were not appreciably different after aging for periods which varied from 1 to 24 hours.

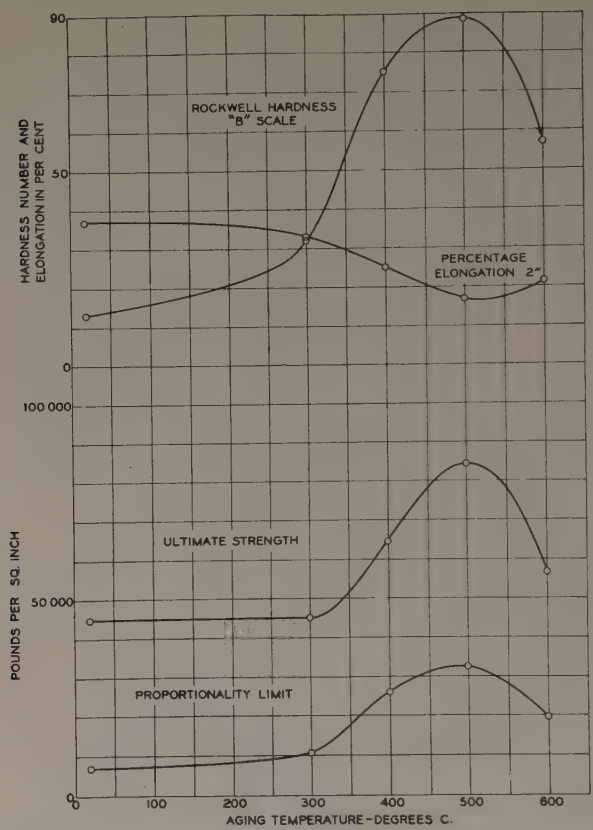

FIG. 3.—EFFECT OF AGING TEMPERATURE ON MECHANICAL PROPERTIES OF NICKEL SILICON BRASS, CONTAINING 9.79 PER CENT. ZN, 2.10 PER CENT. NI AND 0.45 PER CENT SI. SPECIMENS WERE QUENCHED FROM 800° C. AND AGED FOR 1 HR. AT TEMPERATURES SHOWN.

TABLE 3.—*Effect of Time of Aging at 500° C. after Quenching at 800° C. on Mechanical Properties of Nickel-silicon Brass Containing 9.79 Per Cent. Zinc*

Heat Treatment	Rockwell Hardness, "B" Scale, 100-kg. Load	Proportional Limit, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Modulus of Elasticity, Lb. per Sq. In. $\times 10^{-6}$
Quenched from 800° C.; aged 10 min. at 500° C..	80	33,300	77,400	15	16.2
Quenched from 800° C.; aged 1 hr. at 500° C.....	88	32,200	84,600	16	17.8

In a preliminary study, specimens of the 20 per cent. zinc alloy were quenched from 800° and 850° C. and subsequently aged at 500° C. for 1 hr. The specimen quenched from 850° C. had somewhat superior properties, as a whole, in the hardened condition. Consequently, the specimens of this composition were quenched from 850° C. and aged at temperatures from 300° to 600° C. The results are shown in Fig. 4.

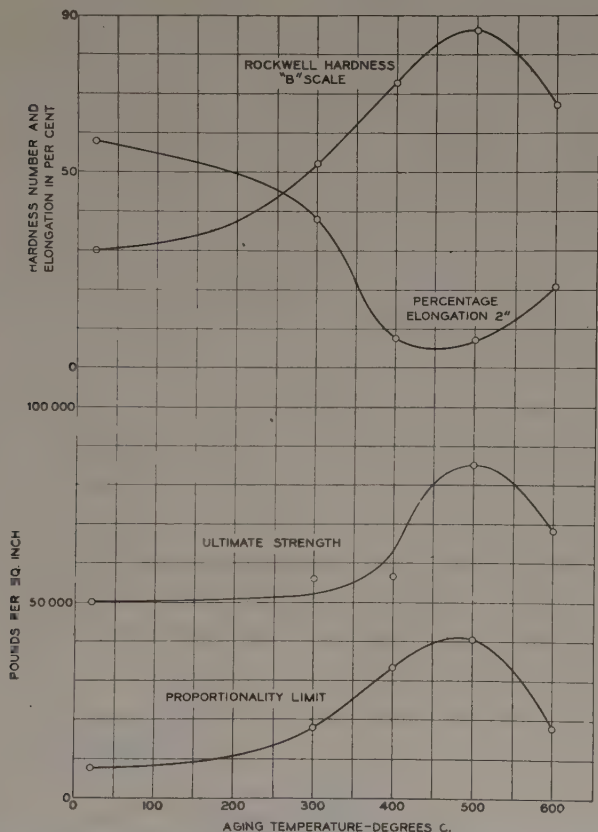

FIG. 4.—EFFECT OF AGING TEMPERATURE ON MECHANICAL PROPERTIES OF NICKEL-SILICON BRASS, CONTAINING 19.58 PER CENT. ZN, 2.54 PER CENT. NI AND 0.68 PER CENT. SI. SPECIMENS WERE QUENCHED FROM 850° C. AND AGED FOR 1 HR. AT TEMPERATURES SHOWN.

As in the case of the 10 per cent. zinc alloy, the best mechanical properties were developed by aging for 1 hr. at 500° C.

The alloy containing 30 per cent. of zinc when quenched from 800° and 850° C., and subsequently aged at 500° C. for 1 hr., developed approximately the same tensile properties. The lower quenching temperature was chosen for subsequent studies. Fig. 5 shows the effect of aging at temperatures from 300° to 600° C. on the properties of this alloy after

quenching from 800° C. It will be observed that the best values were obtained by an aging for 1 hr. at 400° C.

The averages of the tensile values for four specimens of each composition, heat-treated to give the best combination of properties, are summarized in Table 4. Anaconda electrolytic zinc was used in preparing these alloys.

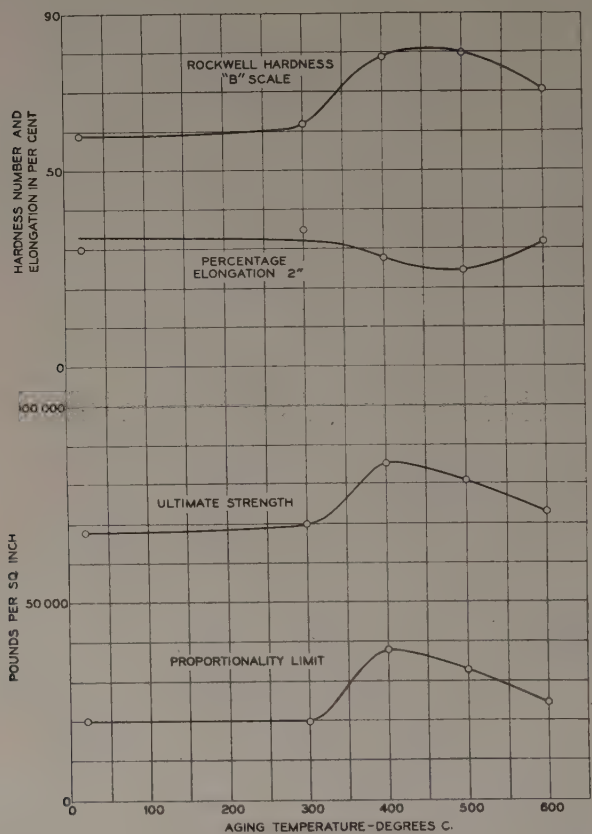

FIG. 5.—EFFECT OF AGING TEMPERATURE ON MECHANICAL PROPERTIES OF NICKEL-SILICON BRASS, CONTAINING 30.12 PER CENT. ZN, 2.36 PER CENT. NI, AND 0.66 PER CENT. SI. SPECIMENS WERE QUENCHED FROM 800° C. AND AGED FOR 1 HR. AT TEMPERATURES SHOWN.

The proportional limit, the ultimate strength and the hardness of these alloys in the heat-treated state compare favorably with values obtained with high-brass sheet in the harder tempers. The moduli of elasticity of the several compositions are appreciably higher resulting in an increased resistance of the materials to elastic deflection. That the ductility of this class of alloys is much greater than that of spring brass is evident on comparing the figures in Table 4.

TABLE 4.—*Tensile Properties of Heat-treated Nickel-silicon Brass*

Material No.	Composition			Heat Treatment	Rockwell Hardness, "B" Scale, 100-kg. Load	Proportional Limit, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Modulus of Elasticity, Lb. per Sq. In. $\times 10^{-6}$
	Zn, Per Cent.	Ni, Per Cent.	Si, Per Cent.						
33	9.89	2.32	0.57	Quenched from 800° C.; aged 1 hr. at 500° C.	86	44,500	90,000	14.0	19.8
34	19.89	2.37	0.57	Quenched from 850° C.; aged 1 hr. at 500° C.	85	37,200	85,800	21.5	17.2
35	30.12	2.36	0.66	Quenched from 800° C.; aged 1 hr. at 400° C.	79	38,000	85,400	28.0	16.5
High-brass Sheet[a]	35.00 (Nominal)			20 B. & S. gage; 10 Nos. hard.	88	33,800	92,700	3.5	14.0[b]

[a] H. N. Van Deusen, L. I. Shaw and C. A. Davis: *Loc. cit.*
[b] Average value obtained as result of tests in Bell Telephone Laboratories.

EFFECT OF COLD ROLLING AFTER HEAT TREATMENT ON PROPERTIES OF NICKEL-SILICON BRASS

Sheets of nickel-silicon brass, 18 B. & S. gage (0.040-in.), the properties of which are recorded in Table 4, were heat-treated to give optimum mechanical properties and subsequently cold-rolled to 24 gage (0.020-in.) sheets. The mechanical properties, determined for these materials in this condition, are compared in Table 5 with values previously obtained for heat-treated sheet.

TABLE 5.—*Effect of Cold Rolling after Heat Treatment on Properties of Some Hardenable Brasses*

Material No.	Composition			Condition	Rockwell Hardness, "B" Scale, 100-kg. Load	Proportional Limit, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Modulus of Elasticity, Lb. per Sq. In. $\times 10^{-6}$
	Zn, Per Cent.	Ni, Per Cent.	Si, Per Cent.						
33	9.89	2.32	0.57	Heat-treated*	86	44,500	90,000	14.0	19.8
33	9.89	2.32	0.57	Heat-treated Cold-rolled	97	43,800	113,700	2.5	14.6
34	19.89	2.37	0.57	Heat-treated*	85	37,200	85,800	21.5	17.2
34	19.89	2.37	0.57	Heat-treated Cold-rolled	98	33,850	111,200	3.0	14.5
35	30.12	2.36	0.66	Heat-treated*	80	33,700	81,400	22.1	16.8
35	30.12	2.36	0.66	Heat-treated Cold-rolled	96	29,550	108,300	3.0	13.8
35	30.12	2.36	0.66	Heat-treated†	79	38,000	85,400	28.0	16.5
35	30.12	2.36	0.66	Heat-treated Cold-rolled	98	39,500	118,500	2.0	14.4

* Aging temperature, 500° C.
† Aging temperature, 400° C.

Strain hardening increases the hardness approximately 15 Rockwell numbers and the ultimate strength from 25 to 40 per cent. The proportional limits in three cases are appreciably less. Material 35, aged at 400° C., shows an increase in proportional limit. A comparison of the moduli values obtained for the heat-treated, and heat-treated and cold-rolled specimens indicates that cold rolling reduces the modulus of elasticity of the heat-treated material.

Structure of the Alloys

Figs. 6, 7 and 8 are photomicrographs of sections of the nickel-silicon brass containing 30 per cent. of zinc in the quenched, and quenched and

Fig. 6.—Nickel-silicon brass containing 30.12 per cent. Zn, 2.36 per cent. Ni and 0.66 per cent. Si. Quenched from 800° C.; twinned structure consisting of small grains. × 100.

aged condition. A solution of ammonium hydroxide and hydrogen peroxide was used for etching. The sections present typical twinned structures. The finely dispersed dark inclusions in the crystals would indicate the presence of a second constituent. That this is the constituent responsible for the change in properties seems unlikely since it occurs in both the quenched and quenched and aged structures.

The crystal size as shown in Fig. 6 is much smaller than would be expected in a brass heated to 800° C., and corresponds more nearly to that developed by annealing at 600° C. Nickel and silicon apparently inhibit crystal growth in these alloys.

Fatigue Characteristics of Nickel-silicon Brass

The fatigue characteristics in reversed bending of heat-treated nickel-silicon brass alloys containing 10, 20 and 30 per cent. of zinc are now being investigated. Results thus far obtained indicate that the endur-

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Fig. 7.—Same specimen as in Fig. 6; showing structure in greater detail. × 350.

Fig. 8.—Specimen of same composition as shown in Figs. 6 and 7, Quenched from 800° C. and aged 1 hr. at 450° C. × 350.

ance limits of these materials are not much different from the values obtained in the case of high brass sheet[4] in the harder tempers when tested under the same conditions in the same type of machine.

[4] J. R. Townsend: Telephone Apparatus Springs. *Trans.* Am. Soc. Mech. Engrs. *Reprint*, Dec., 1928.

Hardening by Heat Treatment of Phosphor-bronze Alloys Containing Nickel and Silicon

The effect of heat treatment on the properties of phosphor-bronze alloys containing 3 per cent. of nickel plus silicon, and 4 and 8 per cent. of tin, respectively, is shown in Table 6. As in the case of the nickel-silicon brasses, the hardness of these alloys can be varied by suitable heat treatments. The maximum hardness values are very nearly the same as those obtained with the same percentages of nickel and silicon in brass.

Table 6.—*Effect of Heat Treatment on Hardness of Two Phosphor-bronze Alloys Containing Nickel and Silicon*

Material No.	Composition					Rockwell Hardness, "B" Scale, 100-kg. Load		
						Quenched from 800° C.	Quenched from 800° C.	
	Cu, Per Cent.	Sn, Per Cent.	Ni, Per Cent.	Si, Per Cent.	P, Per Cent.		Aged 1 Hr. at 400° C.	Aged 1 Hr. at 500° C.
1	92.93	3.88	2.33	0.58	0.37	55	78	80
2	88.40	7.76	2.37	0.59	0.40	64	79	78

The data given in Table 7 indicate the tensile properties which may be expected in some heat-treated phosphor bronze alloys containing nickel and silicon. The values for hardness, proportional limit, and tensile strength are not so high as those obtained with similar alloys rolled to the harder tempers, but containing no nickel and silicon. These results, however, are essentially preliminary, and are included only to indicate that the properties of these alloys can be varied by heat treatment. Alloys with better tensile properties might be expected to result from a change of the nickel and silicon content.

Table 7.—*Properties of Some Heat-treated Phosphor-bronze Alloys Containing Nickel and Silicon*

Material No.	Heat Treatment	Rockwell Hardness, "B" Scale, 100-kg. Load	Proportional Limit, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Modulus of Elasticity, Lb. per Sq. In. $\times 10^{-6}$
1*	Quenched from 800° C.; aged 1 hr. at 500° C...	80	37,900	73,000	22	17.5
2	Quenched from 800° C.; aged 30 min. 500° C...	80	31,000	74,100	22	18.6

* Analyses given in Table 6.

Dispersion Hardening in Nickel-silicon Brass and Bronze

The hardness values of the alloys resulting from different heat treatments are summarized in Table 8. The hardness in the quenched condition increases with the percentage of zinc present. This hardness is probably for the most part a solid solution hardness and would in general be expected to increase with the percentage of solute atoms in the alloy. That the effect of the different atoms in producing hardness is not additive is clearly evident in the case of brass. Bassett and Davis[5] have found that the addition of zinc to copper increases the hardness of the annealed alloys to a Rockwell "B" of 10 numbers at a composition of 25 per cent. of zinc. From this point the hardness decreases to the composition at which the beta constituent begins to appear. The addition of a constant percentage of nickel silicide to the copper-zinc alloys results, however, in a hardness increasing with the percentage of zinc.

It is possible that the percentage of nickel and silicon in these alloys may exceed the solubility limit of these elements in the alpha solid solution at the quenching temperature. If this is the case, a hardening effect would be expected as a result of the second phase. Not enough information is available on the solubility relations in this system to decide whether or not this factor exists.

Table 8.—*Effect of Zinc and Tin Content on Hardness of Nickel-silicon Brass and Bronze*

Composition				Rockwell Hardness, "B" Scale, 100-kg. Load		
Zn, Per Cent.	Sn, Per Cent.	Ni, Per Cent.	Si, Per Cent.	Quenched	Quenched and Aged	Increase
		2.36	0.58	0	85	85
9.89		2.32	0.57	15	88	73
19.89		2.37	0.57	30	86	56
30.12		2.36	0.66	59	80	21
	3.88	2.33	0.58	55	87	32
	7.76	2.37	0.59	64	78	14

In some preliminary studies of the effect of time and temperature of aging on maximum hardness, it was found that the aging temperature for maximum hardness decreases as the percentage of zinc is increased. Likewise, at a given temperature the time of aging required to produce the maximum hardness decreases with the percentage of zinc present. These observations lead to the conclusion that the stability of the nickel

[5] W. H. Bassett and C. H. Davis: Physical Characteristics of Commercial Copper-zinc Alloys. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 55.

silicide supersaturated solution decreases as the percentage of zinc increases. This behavior would be expected, since the addition of zinc distorts the copper lattice,[6] which results in an increase in the lattice energy. Consequently it may be argued that the higher the zinc content in the alloy, the less the external energy required to bring about the phase change. The phase change, in this case, may be considered as the divorcement of nickel and silicon from the lattice.

Further interesting data in connection with the general theory of age hardening would result from an investigation of the effect of different percentages of nickel silicide on the characteristics of the alloys. Such an investigation would also extend the limits of useful alloys in this field.

Summary

1. The mechanical properties of copper-zinc alloys containing nickel and silicon in both the cast and rolled condition can be varied over a wide range by suitable heat heatment. The response to heat treatment in the cast condition suggests that these alloys may have possibilities in the manufacture of high-strength brass castings. The proportional limit, the ultimate strength and hardness of these alloys in the rolled and heat-treated condition are approximately the same as values obtained for spring brass sheet containing a nominal 35 per cent. of zinc. The moduli of elasticity for the several compositions are appreciably higher and the ductility, as evaluated by elongation, much greater than values obtained for spring brass sheet.

These alloys have another desirable property. The hardening is brought about, not by cold rolling, but by a heat treatment. This would permit forming operations on the manufactured part to be performed on the soft material. The desired hardness and strength can be secured by a subsequent heat treatment. Spring brass, phosphor bronze and nickel-silver are shaped, of necessity, in the cold-rolled state. In parts involving sharp bends this may result in severe local overstrain.

2. Further increase in the tensile strength and the hardness of these alloys results from cold rolling the heat-treated material. The proportional limit is not much affected by the subsequent rolling, but the modulus of elasticity is effectively lowered.

3. Incomplete tests of the fatigue behavior in reversed bending of heat-treated nickel-silicon brass alloys indicate an endurance limit not much different from that of high-brass sheet.

4. The mechanical properties of copper-tin alloys containing nickel and silicon can be varied by heat treatment. The preliminary results indicate the possibility of developing useful alloys of this type.

[6] The addition of 38.7 per cent. of zinc alters the parameter of the copper lattice from 3.60 Å to 3.696 Å. E. A. Owen and G. D. Preston: X-ray Analysis of Zinc-copper Alloys. *Proc.* Phys. Soc. London (1923) **36**, 49.

ACKNOWLEDGMENTS

The authors are greatly indebted to J. R. Townsend under whose direction the mechanical tests were made, and to E. J. Basch who aided materially in obtaining the data on the hardenable nickel-silicon bronze alloys.

DISCUSSION

T. S. FULLER, Schenectady, N. Y.—While reading this paper two questions occurred to me: (1) What is the effect of time at the quenching temperature on the mechanical properties of these alloys, and (2) would it not be well to include in the tables the properties of the alloys of copper containing the same amount of nickel and silicon and similarly treated?

J. R. TOWNSEND, New York, N. Y. (written discussion).—In connection with this paper by two of my associates, it may be of interest to report the fatigue endurance limits of the copper-zinc alloys hardened by the addition of nickel and silicon and also that of high-brass sheet. The chemical composition of high-brass sheet is nominally 65 per cent. copper and 35 per cent. zinc and compares closely in composition with alloy No. 35 in the paper under discussion. Table 9 repeats the physical properties of these alloys and gives the endurance limit as determined on specimens of sheet approximately ⅜ in. wide and 3 in. long. Specimens that endured a maximum stress in alternate flexure for 100,000,000 cycles were considered to have reached their endurance limit. The stress was calculated using the value of modulus of elasticity determined from a load deflection curve made for the specimens under test.

It will be noted that the endurance limit for alloy 35 in the heat-treated and aged condition is 33 per cent. higher than annealed high-brass sheet and 17 per cent. higher than high-brass sheet rolled 10 B. & S. numbers hard.

TABLE 9.—*Fatigue Endurance and Related Properties of Brass Sheet*

Material	Temper.	Ultimate Strength, Lb. per Sq. In.	Rock. Hardness "B" Scale	Proportional Limit Lb. per Sq. In.	Elongation in 2 In. Per Cent.	Modulus of Elasticity	Fatigue Limit, Lb. per Sq. In.
Cu 65, Zn 35—High-brass sheet	0	46,600	16	12,000	58	14	12,000
Cu 65, Zn 35—High-brass sheet	10	95,600	87	30,000	2	14.7	13,600
Alloy 33	Quenched 800° C. Aged 1 hr. at 500° C.	90,000	86	44,500	14	19.8	14,000
Alloy 34	Quenched 850° C. Aged 1 hr. at 500° C.	85,800	85	37,200	21.5	17.2	13,000
Alloy 35	Quenched 800° C. Aged 1 hr. at 400° C.	85,400	79	38,000	28.0	16.5	15,900

C. S. Smith, Waterbury, Conn.—Have the authors investigated the effect of cold work on the alloys after the high-temperature quenching, before the precipitation heat treatment? It appears from some preliminary work that I have carried out that cold working at this stage reduces the temperature at which maximum hardness occurs, and, if carried out to a sufficient extent, will cause precipitation to occur even at room temperature. I have observed this particularly in a binary copper-silicon alloy, in which the maximum hardening occurred when the quenched alloy was reannealed at 450° C. After reducing 8 per cent. in thickness, the peak in the curve occurred at 350° C., while after 50 per cent. reduction the alloy did not harden on annealing but immediately commenced to soften. The X-ray diffraction pattern showed several lines due to the γ copper-silicon constituent (Cu_5Si) superimposed on those due to the α solid solution lattice, indicating that fairly complete precipitation had occurred. Precipitation at room temperature is a possible explanation of Mr. Gregg's observation[7] that most age-hardening alloys harden very rapidly on cold working.

W. C. Ellis and E. E. Schumacher (written discussion).—Mr. Fuller has raised an interesting point in connection with the effect of time at the quenching temperature on the properties of the alloys. The results given in this paper are for alloys heated at the quenching temperature for 15 min. In a preliminary study, however, the Rockwell hardness values were determined after heating for 15 min., 30 min., 1 hr. and 2 hr. prior to quenching. The results, shown in Table 10, together with the hardness values resulting from subsequent aging of the quenched material, indicate rather constant hardness independent of the time at the quenching temperature. This is indicative, although by no means conclusive, that the other properties, in the case of these alloys, would be constant with time held at the quenching temperature.

In answer to Mr. Fuller's second question, since the investigation was confined to a study of the properties of zinc-containing alloys, we have no data on nickel-silicon copper for direct comparison. A comparison with the data of Corson[8] for nickel-silicon copper, however, indicates that the addition of zinc does not have much effect on the tensile properties in the hardened condition.

Mr. Smith has emphasized one of the most interesting phases of this investigation; namely, the combined effect of hardening by dispersion and by mechanical strain. We have made a study of the effect of mechanical strain on the properties of the alloy containing 30 per cent. of zinc after quenching as well as after quenching and aging. The alloy hardened very rapidly in the quenched state with cold work. After reduction 10 B. & S. gage numbers the 0.020-in. sheet had reached the hardness values obtained on fully heat-treated sheet, but not the values obtained through cold rolling heat-treated sheet a corresponding reduction. The question naturally arises as to whether part of this hardness is not due to a precipitation from the supersaturated solid solution brought about by the mechanical strain. In some subsequent studies of some similar dispersion-hardening alloys in the form of hard-drawn wire, aging was actually found to occur at room temperature. We plan to discuss this interesting point more completely in a later paper.

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[7] See page 409.

[8] M. G. Corson: Copper Alloy Systems with Variable Alpha Range and Their Use in the Hardening of Copper. *Proc.* Inst. Metals Div., A. I. M. E. (1927) 435.

TABLE 10.—*Effect of Time at Quenching Temperature on Hardness of Some Nickel-silicon Brasses*

Quenching Temperature 800° C.

Material No.	Composition			Time at Quenching Temperature	Rockwell Hardness "B" Scale; 100-kg. load	
	Zn, Per Cent.	Ni, Per Cent.	Si, Per Cent.		As Quenched	Subsequently Aged[a] 1 hr.
33	9.89	2.32	0.57	15 min.	37	88
				30 min.	33	88
				1 hr.	38	88
				2 hr.	33	86
34	19.89	2.37	0.57	15 min.	54	87
				30 min.	50	87
				1 hr.	52	87
				2 hr.	52	87
35	30.12	2.36	0.66	15 min.	54	84
				30 min.	52	84
				1 hr.	54	84
				2 hr.	50	83

[a] Nos. 33 and 34 were aged at 500° C. No. 35 was aged at 400° C.

Diffusion of Zinc into Copper

By Samuel L. Hoyt,* Schenectady, N. Y.

(Philadelphia Meeting, October, 1928)

This paper gives a brief description of an investigation made several years ago on the diffusion of zinc into copper. The material for that study was furnished in the form of thin copper strips coated with zinc. The result was required rather quickly and at not too great an expense, and especially information was desired as to the rate at which zinc would diffuse from the zinc coating into the copper and the temperature at which the operation should be carried out.

A study of the requirements of this problem indicated that the solution might be secured by means of six determinations. This is the smallest number that will give the information desired and, at the same time, furnish checks on the accuracy of the determinations which justify an abbreviated experimental program. This does not count a preliminary test which was designed to give some idea of the correct temperature to use.

The minimum number of temperatures that can be used is two. Knowing the rates of diffusion of zinc into copper at two properly chosen temperatures, it is possible to calculate the rate for any other temperature, and also to check the accuracy of the determination by means of the heat of diffusion, which is calculated from the effect of temperature on the rate of diffusion. The minimum number of determinations at any one temperature is three. The amount of diffusion which occurs at a fixed temperature is definitely related to the time of diffusion, so that by determining the amount of diffusion for three different time intervals, this relationship may be established and possibly a check on the accuracy may be secured. This accounts for the six determinations or experiments, and suggests the logical plan of the work. The check used here is not generally applicable to diffusion phenomena, but it seems to hold closely enough for the limited amount of diffusion in this investigation to justify its use.

The samples used were 5 to 6 mils thick and about 1 in. square. They were placed between iron blocks and set in the hot zone of a nichrome furnace which had been brought to the desired temperature. Time was taken from the moment the samples reached the furnace

* Research Laboratory, General Electric Co.

temperature. After the samples had remained in the furnace for the correct time, they were removed and cooled quickly to room temperature. The amount of penetration of the zinc into the copper was found by examining microsections of the strips. For this measurement, the thickness of the unalloyed copper was subtracted from the initial thickness, and divided by two. The temperatures, times, and penetrations are given in Table 1.

TABLE 1.—*Diffusion of Zinc into Copper*

Time	Temperature, Degrees Cent.	Penetration, Mm.
1 hr.	550	0.75×10^{-2}
2 hr.	550	1.25×10^{-2}
4 hr.	550	3.4×10^{-2}
1 min.	650	0.9×10^{-2}
3 min.	650	1.0×10^{-2}
18 min.	650	2.3×10^{-2}

The solutions of the problem are given in Figs. 1 and 2. In Fig. 1 the log of the penetration is plotted against the time the sample was at

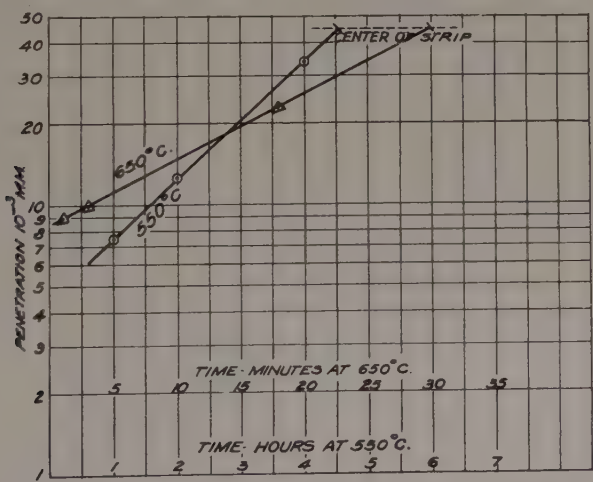

FIG. 1.—PENETRATION OF ZINC INTO COPPER STRIP.

temperature, by means of semilog paper. It will be observed that the points fall on straight lines. One line gives the penetration at 550° C. and the other, the penetration at 650° C. The time required to convert the whole strip into brass, or for the zinc to diffuse to the center of the strip, is obtained by extrapolation. The time is 4½ hr. at 550° C., or 30 min. at 650° C. It is tacitly assumed that the rate of penetration does not change over the small distance remaining, or that the time

rate of change of the rate of penetration remains constant. The time required to produce smaller penetrations would be obtained by interpolation, a process which is less open to criticism than the former. It did not seem important, at the time, to check the accuracy of the times obtained by extrapolation.

In Fig. 2 the effect of temperature on the time required to produce a given penetration is plotted. Here the time estimated for zinc to diffuse to the center of the strip is plotted against the reciprocal of the absolute

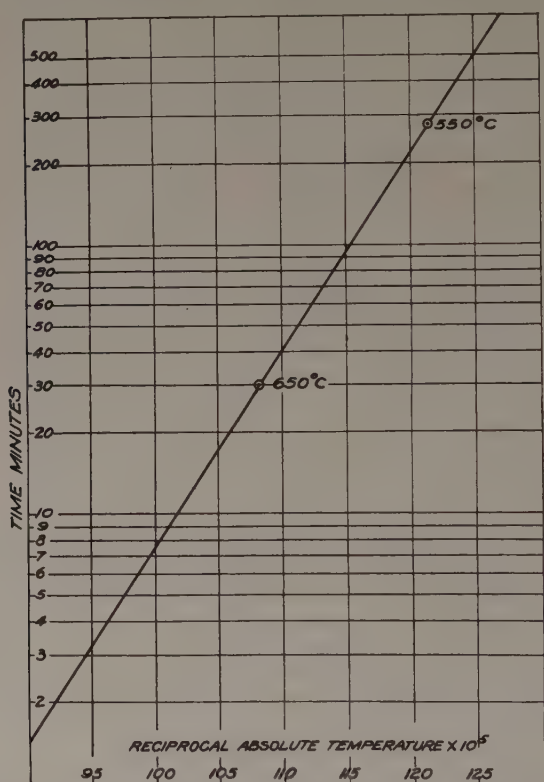

FIG. 2.—TIME VS. TEMPERATURE FOR DIFFUSION OF ZINC TO CENTER OF 0.004-IN. COPPER STRIP.

temperature, the former on the logarithmic scale. By drawing a straight line through the two points, the entire time-temperature relationship is obtained. In the same way we could plot the times corresponding to any smaller penetration. A check on the accuracy is obtained, in this case, by a calculation of the temperature coefficient of the rate of diffusion, or from the heat of diffusion, which can be calculated from the slope of the line. The temperature coefficient was found to be 1.25 for a 10° rise in temperature, while the heat of diffusion came 33,000 calories per gm.-

mol. Both of these values are reasonable and indicate that the measured effect of temperature in this work is approximately correct.

It is obvious that with the data of Figs. 1 and 2, the time and temperature requirements for converting these copper strips into brass, either in whole, or in part, can be readily estimated.

The curves of Fig. 1 are not of the conventional type, since the rate increases instead of decreasing with time. This circumstance suggests that we are dealing with an effect corresponding to an incubation period. The reason for this is not clear, either from the literature, or from the work itself. Even so, the small extrapolation used in solving the present problem seems to be justified on purely empirical grounds, while interpolation to smaller amounts of diffusion would be even more justified. In the light of the findings of this investigation, it would seem that a more detailed study of the diffusion of zinc into copper, and a comparison with other simple types of diffusion, will yield interesting information on metallic behavior.

Acknowledgment

The author extends his thanks to Mary R. Andrews, of the Research Laboratory of the General Electric Co., for her helpful criticism of this work.

DISCUSSION

F. Keller, New Kensington, Pa.—Dr. Hoyt's paper is of considerable interest to us as we have been doing some work along similar lines. Alclad 17ST, a product of the Aluminum Company of America, offers an excellent material for the study of diffusion in the solid state. This product consists of a core of a heat-treatable aluminum alloy with a coating of very pure aluminum on each surface. This high-purity aluminum coating renders the duralumin-type alloys highly corrosion resistant. During the manufacture of the product it is necessary to heat-treat in order to develop the high strength of the core and this heat treatment results in the formation of a diffusion zone in the pure aluminum coating due to the migration of atoms of copper, magnesium, and silicon from the core into the coating. The diffusion zone is clearly revealed on polished cross-sections when suitably etched and may be readily measured microscopically.

Much work has been done on the rate of diffusion in this alloy during various heat treatments, and we found that in the 14-gage Alclad sheet after a 15-min. heat treatment at 500° C. the diffusion zone was 0.001 in. thick. The thickness of coating on 14-gage Alclad sheet is about 0.004 in. After 15-min. heat treatment the diffusion zone was equal to ¼ the coating thickness. However, to cause diffusion to go entirely through the 0.004-in. coating it was necessary to heat-treat for 4½ hr. at this temperature. Curves have been plotted for the rate of diffusion for various heat-treating periods at 500° C. and show that the diffusion is rapid at the beginning, then slows up until the rate of diffusion is fairly small after a period of several hours.

These results are somewhat different from Dr. Hoyt's, inasmuch as he shows the rate of diffusion as very nearly constant. In his case the concentration of the element diffusing was considerably higher than in our material, as our alloy contained only 5 per cent. of soluble elements.

It does seem unusual, however, that the rate of diffusion should remain constant, while the distance from the source of the soluble material increased.

It was our intention to continue this work and we hope to present it in the form of a paper in the near future.

F. H. Clark, New York, N. Y.—Has the condition of the surface of copper and zinc any effect on the rates of diffusion? Would a highly polished surface cause the rate of diffusion to be changed?

D. J. McAdam, Jr., Annapolis, Md.—Some of my questions have undoubtedly been considered by Dr. Hoyt, but I think it would be a good thing to have them in the record.

How is the depth of penetration measured by means of a microscope? The author refers to the time necessary for the zinc to diffuse to the center of the specimen. Does that mean the time for the first atom of zinc to reach the center of the specimen? There is another factor that has to be considered, which was undoubtedly considered by Dr. Hoyt but was not brought out in the paper, and that is the concentration gradient of the zinc. That will change, of course, as the diffusion goes on. After the zinc has reached the center, this concentration gradient would decrease. Even before the zinc reaches the center, it seems to me that the gradient might vary considerably.

As there are possibly several alloys involved, there might be several concentration gradients to be considered. In considering conduction of heat through a metal, we take into account the temperature gradient. It seems to me that in considering the diffusion of one metal into another we have to take into account the concentration gradient.

O. W. Ellis, East Pittsburgh, Pa.—Dr. Hoyt's paper has caused me to think of other ways and means of determining the diffusion of zinc into copper. At the University of Toronto the diffusion phenomenon formed the regular laboratory experiment; every student had to work on the diffusion of zinc into copper. We worked in a different way from Dr. Hoyt, though; we took a copper rod, drilled a hole in it, introduced the zinc into the rod in the molten state and then heated at a series of constant temperatures, not for the quantitative effect, but just for the qualitative effect, to show the difference in rates of diffusion. We made no attempt to measure rates.

It seems to me that there is a method whereby some of the difficulties due to variations in concentration can be overcome, and that is by measuring the distance from a datum point in the unchanged copper to (1) the point at which the first signs of beta constituent appear and (2) to the point at which the alpha disappears. The width of the band of alpha-beta varies during the time the material is held at any given temperature. This variation in width and a knowledge of the distance from the datum point of the points at which the beta starts and the alpha ends will give a very fair basis for a determination of the rate of diffusion of zinc into copper.

With regard to Dr. Clark's question concerning the condition of the surface of the metal, I would like to make mention of one little experiment that I have carried out. I wanted to see what type of coating of aluminum I would get on copper by immersing a rod of the metal in molten aluminum. One ¼-in. rod I took without attempting to clean it; it remained in the aluminum for ½ hr. with apparently no change at all. I took another ¼-in. rod, gave it a dip in nitric acid and a thorough wash. I put it in the aluminum and after five minutes went to look at it, but the rod had disappeared.

Z. Jeffries, Cleveland, Ohio.—This subject of diffusion is important and fundamental in metallurgy and the quantitative elements of it are yet to be worked out

for many systems. The quantitative data given by Dr. Hoyt may be the best so far offered on the zinc-copper system. The quantitative data, however, on the diffusion of thorium in tungsten are probably the most complete of any system of metals.

Some years ago Miss Elam reported experiments dealing with the diffusion of nickel into single-crystal copper. She deposited nickel electrolytically on the surface of a single crystal of copper and was unable to obtain diffusion of the nickel into copper or copper into the coating of nickel by any thermal treatment. The idea became somewhat prevalent that diffusion of one metal in another could not take place in single-crystal form. We have demonstrated, without any possibility of doubt, that this is not true of thorium in tungsten. It is true, however, that fine-grained tungsten will permit the diffusion of thorium within certain selected temperature ranges at least 50 times as fast as in single-crystal tungsten. Nevertheless, diffusion of thorium in a single crystal of tungsten is definite and positive. This is a case, however, of the thorium being already in solution in the tungsten, at least in part, and, therefore, no possibility of surface film obstructions such as were mentioned by Professor Ellis. It has always seemed to me that Miss Elam's experiment might be explained by a surface film between the nickel and the copper.

It would be interesting if Dr. Hoyt would give us some information on the possibility of the diffusion of zinc or any other metal into single-crystal copper or the diffusion of any other substance into any other single crystal.

In Dr. Hoyt's own experiments, he does not mention, I believe, whether the copper strips were annealed prior to the plating with zinc. Of course, this would make a great difference. At the temperatures used, cold-worked copper would recrystallize and the grains would grow at different rates and to different extents at the different temperatures used, and the differences in grain size might account for some of the variations in diffusion. At any rate, knowing what we do about the effect of grain size on the rate of diffusion, that factor should always be taken into consideration.

S. L. Hoyt.—I was interested in Mr. Keller's remarks about the work they are doing on the aluminum-coated product, but I do not believe there is any specific reply called for.

Miss Clark has received a better reply from Professor Ellis than I would be able to give at this time. I took the strips as they were given to me; the surface was reasonably clean and with a fairly good polish produced by a small amount of cold rolling. The surface was certainly not dirty or contaminated.

In reply to Dr. McAdam, the method which I employed for measuring the depth of penetration is given very briefly in the paper. It was a simple matter to determine the amount of copper which had not as yet been penetrated by the zinc, with one reservation, for there was a sharp line of demarcation between the core and the outer layer. I do not believe that that sharp line corresponds to zero per cent. of zinc. It undoubtedly corresponds to some reasonably low percentage of zinc, but it is the point which I used for the determination of the thickness of the outer zone.

The concentration gradient of the zinc was not determined or measured. Of course, that is of very great importance and a complete quantitative study of diffusion would require an estimate or a determination to be made of the concentration gradient. The shape of such concentration curves and the way they vary with time are well known from the literature, but the mathematical difficulties involved in dealing satisfactorily with the change of the concentration gradients with time are altogether too great for any such simple study as this. If you look that up, you will find that it requires a mathematical analysis of rather high order to handle it.

Dr. Jeffries refers to the quantitative data on diffusion and the fact that we really know so much about the diffusion of thorium through tungsten. It would be helpful to have equally complete data about other systems. Certainly this paper does not

give anything like that amount of information on the diffusion of zinc into copper. What Dr. Jeffries says on the effect of grain size on diffusion is much to the point. Mrs. Andrews (to whom reference is made in my acknowledgment) and I did a little work on the diffusion of nickel into copper. We nickelplated a copper single crystal and then attempted to get the nickel to diffuse into the copper. We were greatly surprised to find that we were not able to make the thing work. Personally, I do not think it was due simply to an impenetrable film on the surface of the copper, although I do not mean that we have excluded that possibility. After a small amount of swaging at an elevated temperature, diffusion took place very readily. The zinc coatings on these copper strips were produced by electrolytic deposition.

As to the condition of the strip, unfortunately I cannot give Dr. Jeffries a satisfactory reply to his question. The material on which I did this work was simply handed to me and the work done was not for the purpose of the presentation of a paper but to give a certain specific answer. Therefore, I had no control over the samples used.

W. M. Peirce, Palmerton, Pa. (written discussion).—There are several points regarding this paper on the diffusion of zinc into copper which might well be given some consideration.

First, the copper-zinc system embraces several constituents or phases. Where this condition exists the diffusion of the two metals into each other actually resolves itself into the diffusion of one element through each of the possible phases. The relative rates of diffusion through the several phases may be such that certain phases cannot exist at certain temperatures. It follows that no simple, continuous relation necessarily exists between temperature and the apparent rate of diffusion which is the resultant of the rates of diffusion through the individual phases. An excellent example of this is the case of iron and zinc which form two distinct intermediate phases. When diffusion of one metal into the other occurs, sometimes one and sometimes both intermediate phases are formed, depending partly on temperature and partly on the purity of the iron.

From this it seems possible that any extrapolation of Fig. 2 may be unjustified and even that the assumption of a straight-line curve between the two determined points may be incorrect.

Second, if the data in Table 1 be plotted on ordinary coordinates and the fourth point, zero time-zero penetration be plotted, it does not appear that the rate of diffusion increases with time as stated. In fact, it is evident, from a casual inspection of Table 1, that the rate of penetration during the first hour is never equalled in the subsequent course of the experiments.

Finally, it may be of interest to note that careful microscopic examination in the writer's laboratory, of a copper-zinc boundary on which diffusion had occurred, showed that copper penetrates the zinc along the grain boundaries well in advance of the conversion of the grains themselves to a constituent rich enough in copper to be distinguishable by its color. This is further evidence that the phenomenon dealt with is not simple.

While the experiments described in this paper doubtless served a useful purpose, it is open to question whether the extrapolations and generalizations based on these six determinations can be safely used in a general way.

S. L. Hoyt (written discussion).—Mr. Peirce's first point is well taken for a general discussion of the reciprocal diffusion of copper and zinc into each other, but the paper dealt with the conversion of a copper strip into brass by the absorption of zinc. The relatively small amount of zinc present (about 20 per cent.) made this problem almost wholly that of the diffusion of zinc into and through alpha brass.

It did not seem necessary to make a separate study of the amount of diffusion that occurred during the heating-up period. This amount is contained in that reported for the first period and is responsible for the relatively large amount of diffusion during that period.

Mr. Peirce's final point again deals with the diffusion of copper into zinc and relates to a phenomenon which is well known in this field, grain boundary diffusion. None of this was observed in the study reported in the paper.

Mr. Peirce seems to have read more into the paper than was intended to be there. The paper describes a simple test of a simple effect, and no attempt was made to draw general conclusions from the results.

Some Practical Aspects of Creep in Zinc*

By W. M. Peirce† and E. A. Anderson,‡ Palmerton, Pa.

(New York Meeting, February, 1929)

Corrugated sheet zinc has been used abroad for a great many years as a roofing material. In this country it has been in use for about 10 years. From the outset it was recognized that zinc sheets required closer spacing of the supporting purlins than steel sheets. Exact data regarding safe maximum fiber stresses were not available, however, and on occasions the span used was excessive and the sheets sagged.

This paper describes both service and laboratory tests to determine safe maximum fiber-stress values for various grades of zinc for use in calculating the proper purlin spacings for any gage and profile under given loading conditions. These tests consist of laboratory loading tests on full-size roof sections over extended periods of time; of actual roof installations erected in conformity with the indications of the laboratory tests and observed over a period of years; of careful determinations of the apparent elastic limit of several grades of zinc, and finally of static tests[1] (so-called creep tests) to determine the rate of flow of zinc under a variety of static tensile stresses at definite temperatures. Certain of the individual tests extended over a period of more than two years.

Experimental Loading Tests on Full-size Roof Sections

Deflection in a corrugated roofing sheet under load may be considered to take place in two stages; an initial bending of the sheet under the load and a slow, permanent flow or creep under continued application of the load. Stresses great enough to produce permanent set when prolonged may produce apparent elastic deformation when applied for only a brief interval.

It is impossible to set a time limit on the duration of stress in actual roof installations. Roofs in industrial locations where dust accumulations are heavy, as in cement plants, are often loaded continuously with

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* Contribution from the Research Division, New Jersey Zinc Co., Palmerton, Pa.

† Chief, Metal Research Division, New Jersey Zinc Co.

‡ Chief Investigator, Metal Section, Research Division, New Jersey Zinc Co.

[1] Static tensile tests, as the name implies, consist of the periodic determination of elongation in specimens subjected to a constant uniform tensile stress (dead-weight loading).

heavy deposits of precipitated dust. In northern latitudes, snow loads may persist, under favorable conditions, for weeks.

It is evident, therefore, that safe permissible spans and loads can be determined only from tests of long duration, in which accurate measurements are made of the rate of flow, or creep, without particular regard to the initial deflection.

Loading tests on roof sections, which were extended over a period of months, furnished the following facts as the basis for a practical test. A continuous load that after 20 days has not produced a total deflection under load of more than 0.75 per cent. of the span will not produce a serious further amount of creep. Actually most of the measurable deflection in excess of the initial occurs in 10 days and the additional 10-day loading period is a factor of safety in the test.

The writers have observed that any set of test conditions which does not produce an excessive rate of creep will not produce an objectionable total deflection.

The loading tests discussed in this paper conform to these considerations. The permissible load and span relationships are those found to produce a deflection of not over 0.75 per cent. of the span in 20 days of continuous loading at a temperature not exceeding 70° F.

Test Methods

In order to keep the test conditions comparable with those existing in actual roofs, the sheets were supported on channels which had the usual flange width for purlins. In all tests, each sheet had an underlapping sheet along each edge to simulate the possible reinforcing effect of side laps. Each test sheet was end-lapped in the normal way, but riveting was considered to be unnecessary, as it does not add materially to the strength except in the case of excessive deflections.

Loading was effected by means of cement bags partly filled with heavy Franklinite sand. The partly filled bags permit easy application and even distribution of the load. Unbagged sand has a tendency to bridge and is awkward to handle.

Deflections were measured on the longitudinal axis of the sheets at the span centers. An excellent datum for the measurements was provided by a bronze wire stretched by weights to constant tension and bearing against the lower edge of the purlins. An accurate measuring device was used, in which proper contact of the measuring points with the wire and sheet are indicated by completion of an electric circuit.

All tests were continued for at least 20 days, and the deflection was measured at 24-hr. intervals. The fact that snow loads can occur only at 32° F. or lower was taken into consideration. Temperature control in the test area was impossible, however, and variations between 32°

and 70° F. had to be tolerated. Any error introduced by this variation acts as a factor of safety in applying the results for snow loading, since any increase in temperature increases the rate of creep.

Minimum Gage and Profile

Before considering the results of the roof-section loading tests, it should be pointed out that in addition to the effect of light loads of long duration, we must consider heavy loads of short duration, such as may be produced by workmen walking over the roof. The latter consideration rules out certain gages of zinc, which otherwise might be satisfactory on short purlin spacings. (Note actual minimum in Fig. 1.)

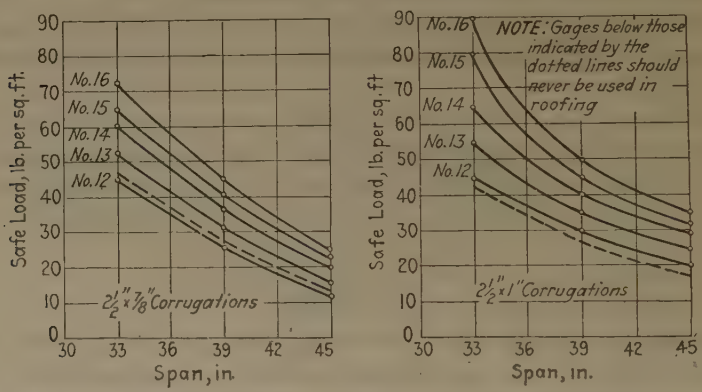

FIG. 1.—SAFE LOAD VERSUS SPAN FOR CORRUGATED ZINC SHEETS.

Permissible Loads and Spans

In Fig. 1 are plotted the permissible load and span relationships developed in this work. The data relate to ⅞ and 1-in. profiles in gages from 12 to 16 inclusive.

Engineering handbooks place the maximum snow and wind load in northeastern United States at 40 lb. per sq. ft. of covering surface uniformly distributed. This value has been adopted by the present writers as a *minimum* load for safe calculations for all localities, as the tendency of a sheet to sag under its own weight and dust loads in hot climates or in hot industrial buildings (as over furnaces) approximates the tendency to sag under a 40-lb. load at freezing temperatures. The safe spans for various profiles and gages under a 40-lb. load are compiled in Table 1.

Since these data were developed, a number of roofs have been constructed, based on these permissible spans. These roofs have been inspected at intervals over a period of years and in no case has sagging been observed.

TABLE 1.—*Permissible Spans for Various Gages and Profiles of Corrugated Zinc Sheets under a 40-lb. Load*[a]

Zinc Gage	Thickness, Inches	Depth of Corrugation, Inches	Permissible Span, Inches
12	0.028	7/8	This gage is not used for roofing
12	0.028	1	34.5
13	0.032	7/8	36.0
13	0.032	1	37.0
14	0.036	7/8	38.0
14	0.036	1	39.5
15	0.040	7/8	39.0
15	0.040	1	41.0
16	0.045	7/8	40.0
16	0.045	1	42.5

[a] End spans (where the reinforcing effect of end laps is absent) should be 80 per cent. of these values.

Calculation of Maximum Fiber Stress under Safe Loads

In order to secure approximate values for the maximum fiber stresses developed in sheets sustaining the safe loads arrived at in the preceding tests, the section modulus of these sheets was approximated as closely as possible and the fiber stress calculated by the formula

$$f = \frac{M}{J}$$

where f is the maximum fiber stress, J is the section modulus and M is the maximum bending moment.

The calculated fiber stresses were found to vary roughly between 4000 and 6000 lb. per sq. in., as shown in Table 2. The average maximum

TABLE 2.—*Fiber Stresses in Corrugated Zinc Sheets of 2½ by 7/8-in. Profile under Safe Loading Conditions*

Thickness, Inches	Load (L), Lb. per Sq. Ft.	Span (S), Inches	J, Lb. per Sq. In.	Fiber Stress (f), Lb. per Sq. In.	$fS^{3/2} \times 10^{-4}$
0.028	47	33	0.0072	6170	117
0.028	26	39	0.0072	4770	116
0.028	12.5	45	0.0072		
0.036	60	33	0.00935	6060	115
0.036	36	39	0.00935	5030	122
0.036	19	45	0.00935	3560	108
0.045	75	33	0.0118	6000	114
0.045	43	39	0.0118	4800	117
0.045	26	45	0.0118	3800	115
Average.....					115

fiber stress under conditions of safe spans for 40-lb. loads was found to be 4700 lb. per square inch.

Table 2 shows that the safe maximum fiber stress is not a constant but varies with the span. From column 6, it appears that $fS^{3/2}$ is a constant as expressed in the equation

$$f = \frac{115 \times 10^{-4}}{S^{3/2}}$$

f = fiber stress;
S = span in inches.

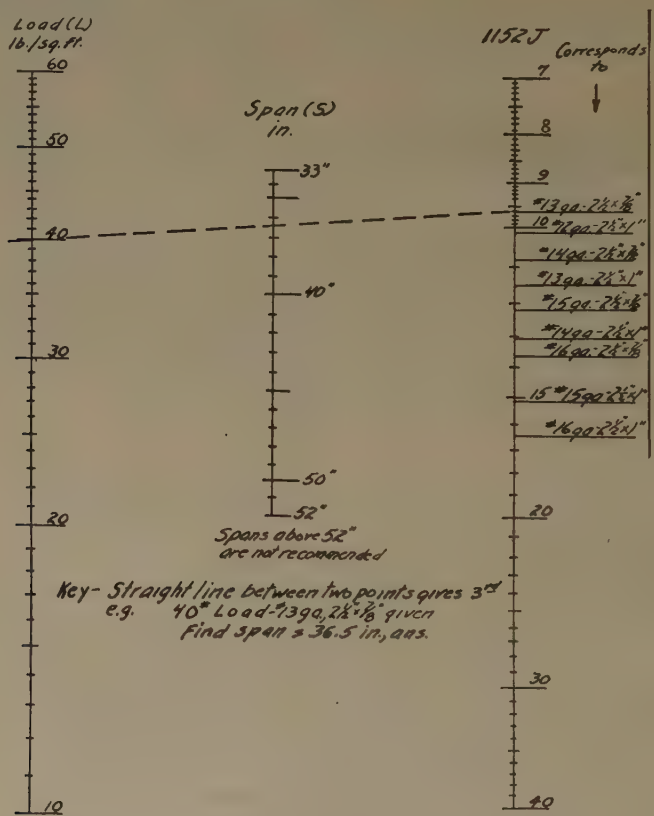

FIG. 2.—LOAD-SPAN DIAGRAM FOR CORRUGATED ZINC SHEETS

Based on formula $\frac{LS^2}{1152J} + 176S = 12{,}100$

The development of this relation makes it possible to predict safe loads for new profiles, gages and spans by the formula

$$\frac{LS^2}{1152J} + 176S = 12{,}100$$

J, of course, must be determined for each new profile. This has been

successfully done in a number of cases. Fig. 2 furnishes a graphical means for applying this formula.

Direct Determination of Safe Maximum Fiber Stress for Zinc

Contemporaneously with the loading tests on roof sections, determinations of the safe maximum continuous stress for zinc were carried out by two other methods. The first method was a very careful determination of the apparent elastic limit, and the second, the measurement of flow (or creep) of tensile specimens under static load.

Apparent Elastic Limit of Zinc

The determination of the elastic limits of soft metals is attended by serious experimental difficulties. In the case of zinc, the influence of rate and duration of loading is so pronounced that what appears to be an elastic reaction at one speed may well be a plastic change at a lower speed. It seemed wiser, therefore, not to attempt the determination of a true proportional limit.

J. B. Johnson's[2] method of obtaining an apparent elastic limit is of value in studying soft metals. This method requires that the apparent elastic limit shall be taken as that stress at which the rate of deformation is 50 per cent. greater than the initial rate. A stress-strain diagram is necessary for this determination. The apparent elastic limit determined by this method is of distinct value in work of this kind because it identifies a boundary between regions of very slow flow and regions of rapid flow.

The present determinations were made under the direction of Prof. H. F. Moore in his laboratories at the University of Illinois. Three grades of zinc were tested, as follows:

Marked	A. S. T. M. Grade	Rolled	Nominal Compositions	
			Pb, Per Cent.	Cd, Per Cent.
A	High Grade	Soft	0.05	0.002
B	Brass Special	Soft	0.3	0.3
C	Prime Western	Soft	0.8	0.15

Specimens were cut with the longitudinal axis in the direction of rolling (marked W) and across this direction (marked A).

The tests were made in a sensitive apparatus using an autographic means of recording the stress-strain curve. Readings were obtained at successive increments of 0.0005 in. of elongation on a 2-in. gage length. Three different head speeds were used, but because of variations in the mobility of the various zincs at different periods of test, it was necessary

[2] A. S. T. M. Tentative Standards (1927) 1075, Method 2.

to determine the rate of flow at rupture and at a point below the Johnson limit. The data obtained in these tests are compiled in Table 3.

TABLE 3.—*Johnson's Elastic Limit in Three Grades of Zinc*[a]

Specimen Marked	Rate of Stretch, In. per In. per Min.		Unit Stress, Lb. per Sq. In.		Elongation, Per Cent. in 2 In.	Temperature, Deg. C.
	Below Johnson Limit	At Rupture	At Johnson Limit	At Rupture		
A-W	0.00027	0.030	4,300	18,800	66	12.5–19.5
A-W	0.00118	0.650	4,000	20,800	49	25.0
A-W	0.0030	0.082	5,300	18,300	64	25.0
A-A	0.00023	0.033	5,400	22,000	40	20.0
A-A	0.0010	0.750	6,300	26,200	36	24.5
A-A	0.0027	0.092	8,000	24,000	34	25.0
B-W	0.00020	0.035	6,200	20,200	38	12.0
B-W	0.00112	0.60	5,200	22,200	35	23.5
B-W	0.00265	0.098	6,500	20,300	35	22.5
B-A	0.000182	0.039	10,200	29,200	26	13.0
B-A	0.000823	0.70	10,200	30,900	22	23.0
B-A	0.00228	0.12	10,000	29,200	24	22.5
C-W	0.000243	0.034	5,200	18,200	49	23.5
C-W	0.00107	0.65	5,800	21,200	43	23.0
C-W	0.0026	0.097	6,000	19,500	33	23.0
C-A	0.000207	0.039	10,300	28,200	20	24.0
C-A	0.00095	0.75	10,500	29,500	14	23.0
C-A	0.00253	0.113	10,500	28,300	19	23.0

[a] All tests average of three specimens.

The material used in the sheet loading tests previously described approximated in composition and rolling treatment the metal marked "C" in Table 3. Inasmuch as the corrugations in a sheet run in the direction of rolling, it is necessary to base comparisons between safe fiber stress and the apparent elastic limit on the data for "C-W."

The safe fiber stress under permissible conditions of load and span was found in the preceding section of this paper to be 4700 lb. per sq. in. The apparent elastic limit of "C-W" at the lowest rate of loading was found to be 5200 lb. per sq. in. It is clearly evident that the Johnson method at once provides a reasonably accurate means of estimating permissible fiber stresses and an excellent confirmation of the load-span relationships shown in Fig. 1.

A number of other interesting points are brought out in Table 3. While these points are foreign to the purpose of this paper, they con-

stitute valuable information on zinc. A brief summary of the more outstanding considerations is given below:

1. The apparent elastic limit is displaced upward by increasing the rate of stretch. This is equivalent to a decrease in mobility with increase in rate of loading at this point.

2. The ultimate breaking stress is increased by higher rates of loading.

3. The elongation at rupture is highest at the low rates of stretch and lowest at the higher rates.

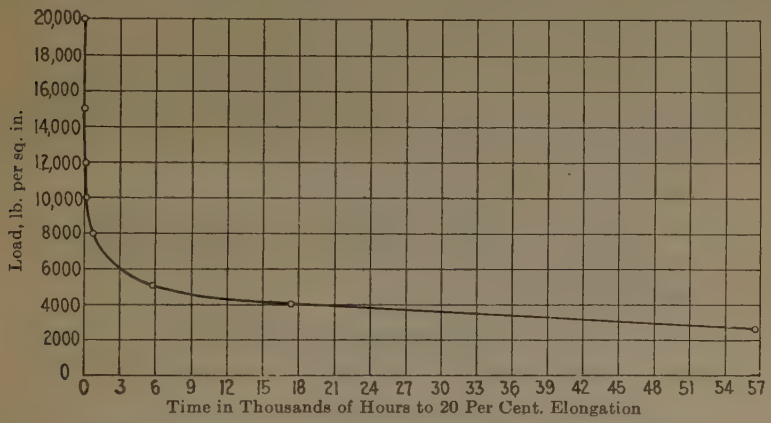

FIG. 3.—TIME TO 10 PER CENT. ELONGATION-LOAD CURVE FOR SOFT-ROLLED BRASS—SPECIAL ZINC LOADED AT ROOM TEMPERATURE (20 TO 30° C.).

4. The apparent elastic limit and the ultimate breaking load are higher in the across-grain direction than in the direction of rolling. The elongation, however, is lower.

It is evident that the effect of rate of loading on the mobility of zinc is not constant throughout the entire stress-strain curve.

STATIC TENSILE TESTS

If tensile specimens of zinc are submitted to a series of static loads and the time necessary to produce 20 per cent. elongation is accurately measured and the respective times are plotted against load, a curve of the type shown in Fig. 3 results.

The interesting feature of this curve is the sharp break at about 5000 lb. per sq. in. Below this load the rate of flow or creep becomes very small and decreases very rapidly with decreasing load. It should be noted that this test was carried out at room temperature, which varied between 20° and 30° C.

It is well known that the ordinary mechanical properties of zinc vary rapidly with small changes in temperature in the range between 0° C. and 40° C. For this reason an extensive series of static tensile tests was carried out at 20° C., 40° C. and 60° C. to determine the effect of

temperature variation on rate of flow. Tests at 0° C. which, of course, require the longest time to complete are not yet available.

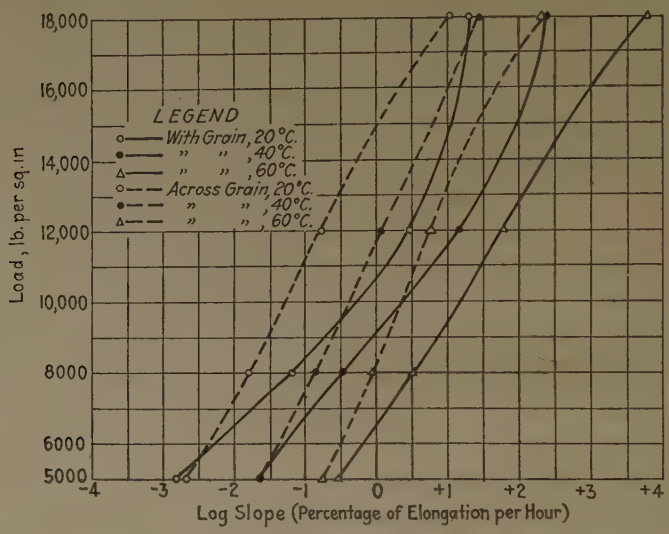

FIG. 4.—LOG SLOPE-LOAD CURVES FOR HOT-ROLLED HIGH-GRADE ZINC (METAL E).

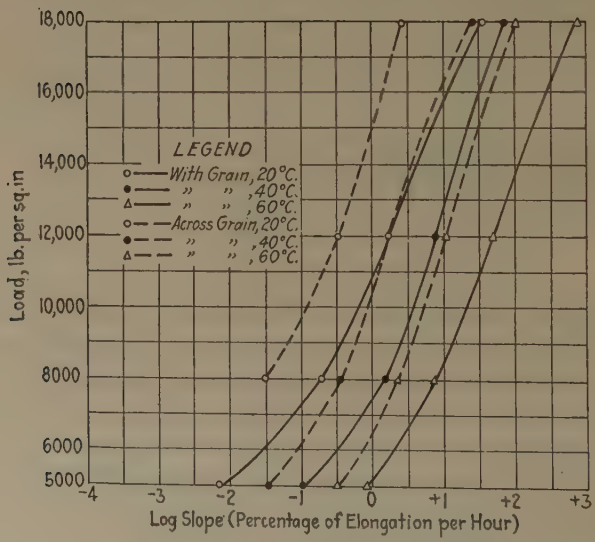

FIG. 5.—LOG SLOPE-LOAD CURVES FOR HARD-ROLLED HIGH-GRADE ZINC (METAL F).

For these tests an inclosed rack was constructed in which nine specimens could be maintained at any temperature between 0° and 85° C. to an accuracy of 1° C. Measurements of elongation were made by means of an accurate optical cathetometer. The metals tested were:

Marked	Nominal Composition		Rolled	A. S. T. M. Grade
	Pb, Per Cent.	Cd, Per Cent.		
E	0.05	0.002	Soft	High Grade
F	0.05	0.002	Hard	High Grade
G	0.3	0.3	Soft	Brass Special
H	0.3	0.3	Medium Hard	Brass Special
I	0.3	0.3	Hard	Brass Special

The method of plotting used in Fig. 3 has obvious disadvantages. One of these is the fact that the rate of flow during the course of a static

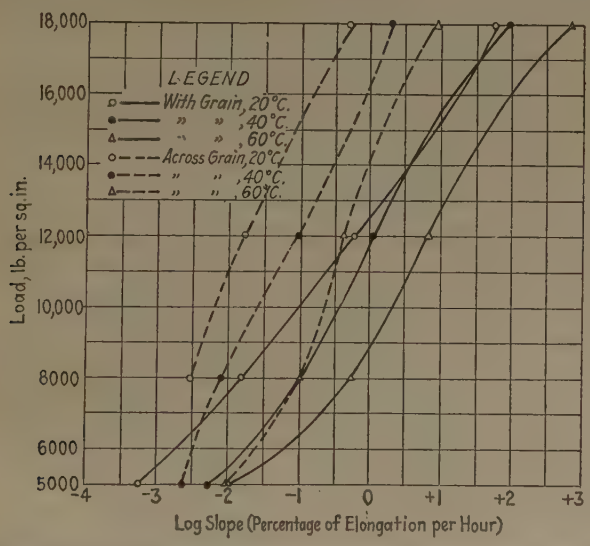

FIG. 6.—LOG SLOPE-LOAD CURVES FOR SOFT-ROLLED BRASS-SPECIAL ZINC (METAL G).

test varies, being somewhat erratic and rapid at the outset and assuming a fairly constant slope thereafter, until the elongation is sufficient to cause necking down. The characteristic feature of any curve is the period of reasonably uniform slope, hence this is the best numerical index of the flow of any specimen. The wide range of values necessitates logarithmic plotting and these results will be found plotted as log rate of flow versus load in pounds per inch in Figs. 4 to 8 inclusive. The data are compiled in Table 4 for purposes of reference.

It has been pointed out that snow loads, which are the most severe loads encountered for any great duration of time, can occur only at or below freezing. Fig. 9, which shows a reasonable extrapolation of the temperature or rate of flow curves to 0° C., indicates that a sheet which has a sufficiently low rate of flow under a load of 5000 lb. per sq. in. at

20° C. to warrant its use under such a stress in roofing sheets would have an indicated safe stress of 8000 lb. per sq. in. at 0° C. Hence, safe loads

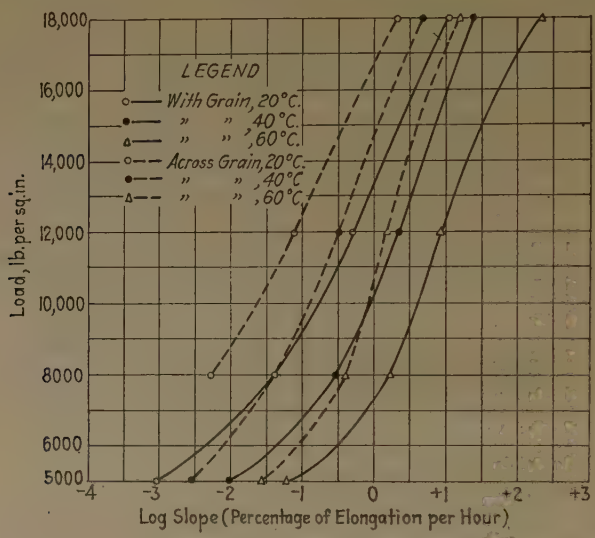

FIG. 7.—LOG SLOPE-LOAD CURVES FOR HARDER ROLLED BRASS-SPECIAL ZINC (METAL H).

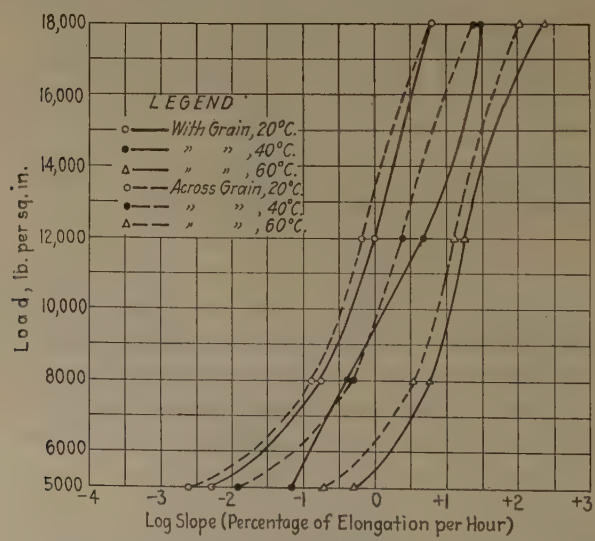

FIG. 8.—LOG SLOPE-LOAD CURVES FOR HARDEST ROLLED BRASS-SPECIAL ZINC (METAL I).

determined at a 20° C. temperature have a factor of safety of about 1.6 for snow-load conditions.

The stresses due to the weight of the sheet itself are less than 1000 lb. per sq. in., giving a high factor of safety at the other extreme of temperature,

TABLE 4.—*Slope and Log Slope of Static Tensile Curves*

Specimen Marked	20° C. Tests								40° C. Tests								60° C. Tests							
	Slope, Per Cent. Elongation per Hour				Log Slope				Slope, Per Cent. Elongation per Hour				Log Slope				Slope, Per Cent. Elongation per Hour				Log Slope			
	5,000	8,000	12,000	18,000	5,000	8,000	12,000	18,000	5,000	8,000	12,000	18,000	5,000	8,000	12,000	18,000	5,000	8,000	12,000	18,000	5,000	8,000	12,000	18,000
E-W.....	0.0015	0.0639	2.83	19.8	$\bar{2}.176$	$\bar{2}.806$	0.452	1.297	0.0215	0.325	15.0	240	$\bar{2}.332$	$\bar{1}.512$	1.176	2.380	0.272	3.334	57.0	6024	$\bar{1}.435$	0.523	1.756	3.780
E-A.....	0.002	0.015	0.165	10.5	$\bar{3}.301$	$\bar{2}.176$	$\bar{1}.217$	1.021	0.023	0.130	1.20	26.7	$\bar{2}.362$	$\bar{1}.114$	0.079	1.427	0.1714	0.862	5.714	206.4	$\bar{1}.234$	$\bar{1}.936$	0.757	2.315
F-W.....	0.0069	0.194	1.6	34.3	$\bar{3}.839$	$\bar{1}.288$	0.204	1.535	0.100	1.50	7.500	70.6	$\bar{1}.000$	0.176	0.875	1.849	0.800	7.50	50.0	720	$\bar{1}.903$	0.875	1.699	2.857
F-A.....	[a]	0.03	0.319	2.52	[a]	$\bar{2}.477$	$\bar{1}.504$	0.401	0.033	0.333	1.710	25.7	$\bar{2}.519$	$\bar{1}.522$	0.233	1.410	0.300	2.309	10.80	100	$\bar{1}.477$	0.363	1.033	2.000
G-W.....	0.00058	0.0155	0.577	54.5	$\bar{4}.763$	$\bar{2}.190$	$\bar{1}.761$	1.736	0.0055	0.100	1.060	85.80	$\bar{3}.740$	$\bar{1}.000$	0.025	1.933	0.0105	0.546	6.024	666.7	$\bar{2}.021$	$\bar{1}.737$	0.780	2.824
G-A.....	[a]	0.00314	0.017	0.49	[a]	$\bar{3}.497$	2.230	$\bar{1}.690$	0.0023	0.0084	0.096	1.850	$\bar{3}.362$	$\bar{3}.924$	$\bar{2}.982$	0.267	0.0094	0.100	0.400	8.426	$\bar{3}.973$	$\bar{1}.000$	$\bar{1}.602$	0.926
H-W.....	0.0009	0.042	0.49	10.9	$\bar{4}.954$	$\bar{2}.623$	$\bar{1}.690$	1.037	0.0092	0.308	2.140	23.10	$\bar{3}.964$	$\bar{1}.489$	0.330	1.364	0.063	1.72	8.576	214.6	$\bar{2}.799$	0.236	0.933	2.332
H-A.....	[b]	0.0052	0.078	2.0	[b]	$\bar{3}.716$	$\bar{2}.892$	0.301	0.0028	0.0414	0.321	5.000	$\bar{3}.447$	$\bar{2}.617$	1.507	0.699	0.027	0.400	1.580	15.02	$\bar{2}.431$	$\bar{1}.602$	0.199	1.176
I-W.....	0.0051	0 175	0.97	6.25	$\bar{3}.708$	$\bar{1}.243$	$\bar{1}.987$	0.796	0.0667	0.428	4.620	30.0	$\bar{2}.824$	$\bar{1}.631$	0.665	1.477	0.500	6.02	17.15	250.0	$\bar{1}.699$	0.780	1.234	2.398
I-A.....	0.0025	0.130	0.705	5.83	$\bar{3}.398$	$\bar{1}.114$	$\bar{1}.848$	0.766	0.0117	0.500	2.400	25.0	$\bar{2}.068$	$\bar{1}.699$	0.380	1.398	0.188	3.53	13.33	109.5	$\bar{1}.274$	0.548	1.124	2.039

[a] No test.

[b] Specimens broke before reaching 5 per cent.

40° C. A dust load of 10 lb. per sq. ft. would give a rise to a maximum stress of 1700 lb. per sq. in. under the safe loading conditions established and at 40° C. this would still allow a factor of safety of about 2.

Summary

Three methods of arriving at a safe maximum working stress have been described in some detail. A fourth, practical experience, which is in most cases the final test of the validity of any engineering deductions, has been mentioned as confirming the results arrived at.

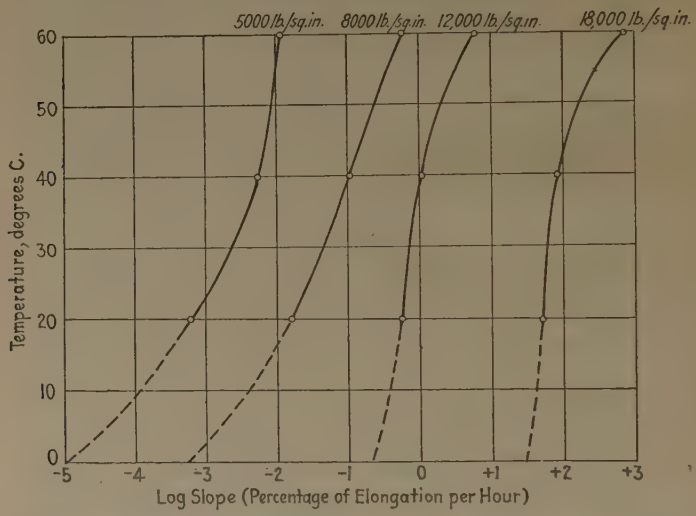

Fig. 9.—Temperature-log slope curves for soft-rolled brass-special zinc (metal G).

The writers believe that this rather practical correlation between laboratory stress data of three types and stresses in satisfactory structures, all leading to a concordant conclusion, is of general interest. Briefly summarized, the tests indicate that:

1. In commercial corrugated zinc-sheet roofs, which have proved satisfactory, the maximum fiber stress under the most severe assumed service conditions is less than 6000 lb. per square inch.

2. Commercial zinc has a Johnson's proportional limit of approximately 5000 lb. per square inch.

3. In static tensile tests (creep tests), a sharp reduction to a very low value occurs in the rate of creep at approximately 5000 lb. per square inch.

Acknowledgment

The writers express their appreciation of the assistance rendered by E. H. Kelton, G. W. Gotherman and G. L. Werley in conducting these experiments, and by Dr. C. H. Mathewson in revising and correcting the manuscript.

Effect of Arsenic on Dispersion-hardenable Lead-antimony Alloys

By K. S. Seljesater,* Chicago, Ill.

(New York Meeting, February, 1929)

Since the development of dispersion-hardenable lead-antimony alloys[1] in the laboratories of the Western Electric Co., Inc., studies have been made of the effect of various third constituents on these alloys.[2] This paper covers a study of the effect of small amounts of arsenic. This element is important since it occurs as an impurity in many commercial antimonial leads and the results obtained are particularly interesting as indicating a class of addition agents which exert a stabilizing effect on dispersion-hardened alloys.

Experimental

In order to study the effect of increasing amounts of arsenic, a series of alloys were made up containing 1 per cent. antimony, and arsenic varying from 0. to 0.10 per cent., the balance Doe Run lead (99.997 per

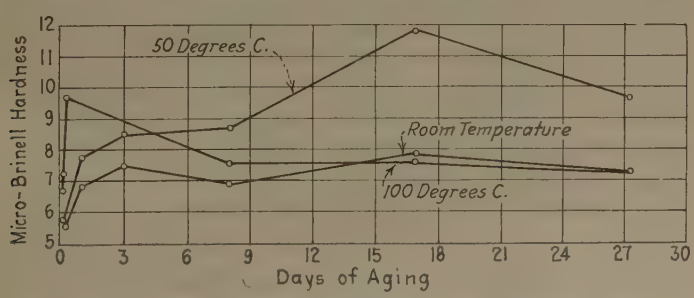

Fig. 1.—Change of micro-Brinell hardness with time of 1 per cent. lead-antimony alloy.

cent. lead). The alloys were cast into bars 1½ in. wide by ¾ in. thick and cold-rolled to about ⅛ in. thickness. Three samples of each composition were annealed 1 hr. at 225° C. and quenched in water. One set was aged at room temperature, one at 50° C., and the third at 100° C., the

* Metallurgical Division, Western Electric Co., Inc.

[1] R. S. Dean, W. E. Hudson and M. F. Fogler: The System Lead-antimony. *Ind. & Eng. Chem.* (1925) **17**, 246.

[2] R. A. Morgen, L. G. Swenson, F. C. Nix and E. H. Roberts: Ternary Systems of Lead-antimony and a Third Constituent. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 316.

aging process being followed by hardness measurements. The results of these tests are shown in Table 1 and Figs. 1, 2 and 3.

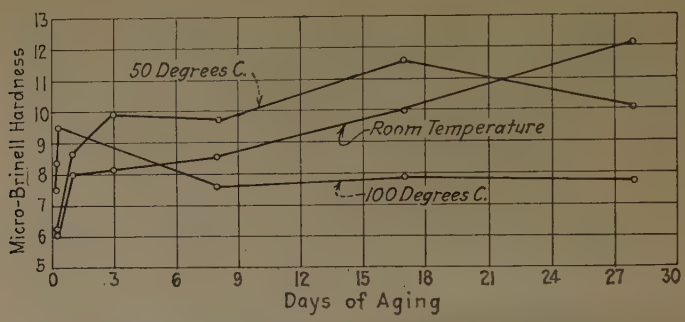

FIG. 2.—CHANGE OF MICRO-BRINELL HARDNESS WITH TIME OF 1 PER CENT. LEAD-ANTIMONY ALLOY CONTAINING 0.01 PER CENT. ARSENIC.

TABLE 1.—*Change of Micro-Brinell Hardness (5-kg. Load; 1/16-in. Ball) with Time of 1 Per Cent. Lead-antimony Alloys to Which Arsenic Has Been Added*

Time (Days)	As, 0 Per Cent.	As, 0.01 Per Cent.	As, 0.03 Per Cent.	As, 0.05 Per Cent.	As, 0.10 Per Cent.
Aging at Room Temperature					
1/4	5.60	6.05	6.50	6.30	6.80
1	6.85	8.00	8.25	8.75	8.75
3	7.50	8.15	9.45	8.90	8.80
8	6.90	8.55	9.90	9.55	8.90
17	7.85	10.05	11.75	11.75	11.70
28	7.25	12.20	11.65	11.25	10.95
Aging at 50° C.					
1/4	5.70	6.25	6.60	6.45	7.0
1	7.80	8.65	9.70	10.0	9.70
3	8.50	9.90	10.45	12.05	11.70
8	8.70	9.75	10.45	11.90	10.55
17	11.85	11.60	12.85	12.50	11.70
28	9.65	10.10	10.15	10.95	10.25
Aging at 100° C.					
1/24	6.70	7.60	8.35	8.65	8.40
1/6	7.30	8.40	9.35	9.50	8.75
1/3	9.70	9.55	9.80	11.45	11.25
8	7.55	7.65	8.20	8.15	8.45
17	7.60	7.90	7.85	8.15	7.90
28	7.25	7.75	7.75	8.15	7.90

At 100° C. aging the effect of arsenic is practically negligible. At 50° C., the aging process is accelerated by the presence of arsenic; however, at the end of 28 days no appreciable difference exists between the samples containing arsenic and the straight 1 per cent. antimony alloy. Under room-temperature conditions the addition of arsenic is apparently

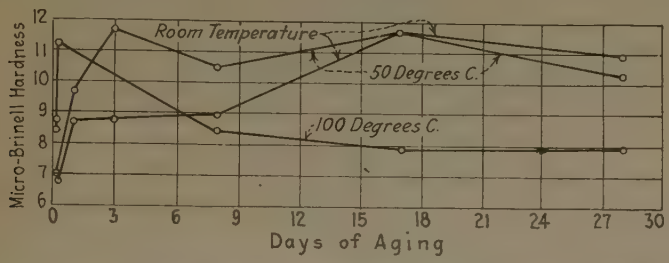

FIG. 3.—CHANGE OF MICRO-BRINELL HARDNESS WITH TIME OF 1 PER CENT. LEAD-ANTIMONY ALLOY CONTAINING 0.10 PER CENT. ARSENIC.

an advantage. The increase in hardness appears to be independent of the amount of arsenic over 0.01 per cent. Without any arsenic the hardness of the 1 per cent. antimony alloy is 7.25 after 28 days of aging; whereas with 0.01 per cent. arsenic the hardness is 12.2 on the micro-Brinell scale.

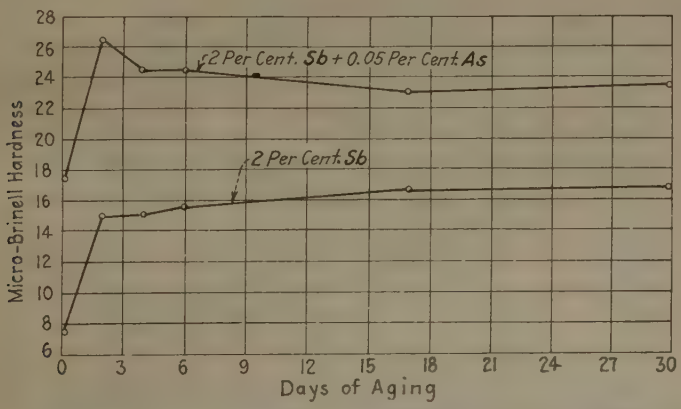

FIG. 4.—CHANGE OF MICRO-BRINELL HARDNESS WITH TIME OF 2 PER CENT. LEAD-ANTIMONY ALLOYS, CONTAINING ARSENIC 0 AND 0.5 PER CENT., RESPECTIVELY; ROOM TEMPERATURE.

Similar experiments were conducted for a series of alloys containing 2 per cent. antimony and arsenic varying from 0 to 1.0 per cent. Three samples of each composition were quenched from 240° C., one set was aged at room temperature, one at 50° C., while the third was exposed to 100° C. for a given period of time. The results are given in Table 2 and Figs. 4 to 6.

TABLE 2.—*Change of Micro-Brinell Hardness with Time of 2 Per Cent. Lead-antimony Alloys to Which Arsenic Has Been Added*

Time	As, 0.0 Per Cent.	As, 0.01 Per Cent.	As, 0.05 Per Cent.	As, 0.07 Per Cent.	As, 0.10 Per Cent.	As, 0.20 Per Cent.	As, 1.0 Per Cent.
Room-temperature Aging							
1½ to 2½ hr.*	7.4	17.4	17.4	14.6	13.0	12.1	11.4
2 days.....	14.9	26.7	26.4	23.4	25.1	25.1	27.0
4 days.....	15.1	24.8	24.5	24.3	24.2	24.5	25.5
6 days.....	15.5	24.6	24.6	24.5	24.2	23.6	23.8
17 days.....	16.6	23.5	23.1	23.1	23.3	23.3	23.1
30 days†.....	16.7	23.6	23.6	23.6	23.3	23.3	23.3
Aging at 50° C.							
2 days.....	16.3	23.6	20.3	22.6	20.9	19.9	20.3
3 days.....	15.2	20.6	20.3	20.6	20.8	18.9	19.4
7 days.....	14.5	19.7	19.1	18.9	19.1	18.1	18.0
17 days.....	13.9	19.2	18.7	18.3	18.5	18.2	18.0
30 days.....	12.9	17.7	17.6	17.5	17.1	16.6	17.6
Aging at 100° C.							
13 days.....	9.0	9.3	8.9	9.2	9.0	9.1	9.3

* Uneven values in this series due to uneven time of aging.

† A somewhat higher maximum value of hardness of 2 per cent. antimony alloy was found earlier, namely 17.5.

The results indicate that addition of arsenic gives a considerable increase in hardness in a dispersion-hardened 2 per cent. lead-antimony alloy when it is aged at room temperature. The decrease of hardness

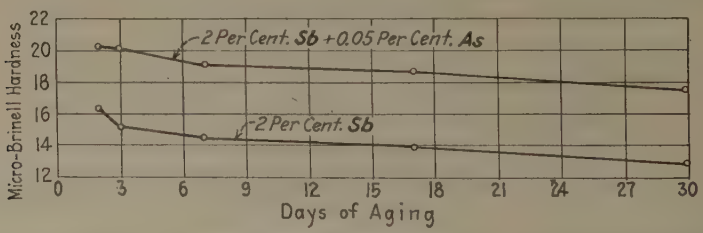

FIG. 5.—CHANGE OF MICRO-BRINELL HARDNESS WITH TIME OF 2 PER CENT. LEAD-ANTIMONY ALLOYS CONTAINING ARSENIC, 0 AND 0.5 PER CENT., RESPECTIVELY; TEMPERATURE, 50° C.

with time is also less at temperatures up to 50° C. The hardness of the alloys after heating to 100° C. is not benefited by the presence of arsenic.

Hardness measurements were also made on 2.5 and 4.0 per cent. antimony alloys containing 0.12 per cent. arsenic as compared with the

same compositions without arsenic. The samples were quenched from 240° C. and aged for 1 week at room temperature. The results are given in Table 3.

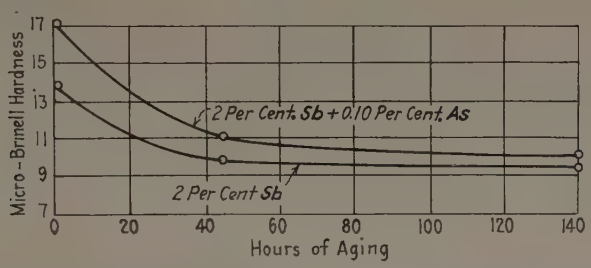

FIG. 6.—CHANGE OF MICRO-BRINELL HARDNESS WITH TIME OF 2 PER CENT. LEAD-ANTIMONY ALLOYS, CONTAINING ARSENIC, 0 AND 0.10 PER CENT., RESPECTIVELY; TEMPERATURE, 100° C.

TABLE 3.—*Micro-Brinell Hardness of* 2.5 *and* 4 *Per Cent. Antimony Alloys Containing* 0 *and* 0.12 *Per Cent. Arsenic, Respectively*

COMPOSITION	MICRO-BRINELL HARDNESS
2.5 per cent. Sb	21.3
2.5 per cent. Sb + 0.12 per cent. As	27.6*
4.0 per cent. Sb	21.5
4.0 per cent. Sb + 0.12 per cent. As	29.0†

* Hardness as cast, 11.0.
† Hardness as cast, 12.9.

Further experiments were conducted in order to ascertain to what the effect of arsenic is due. The lead-rich end of the antimony-lead diagram

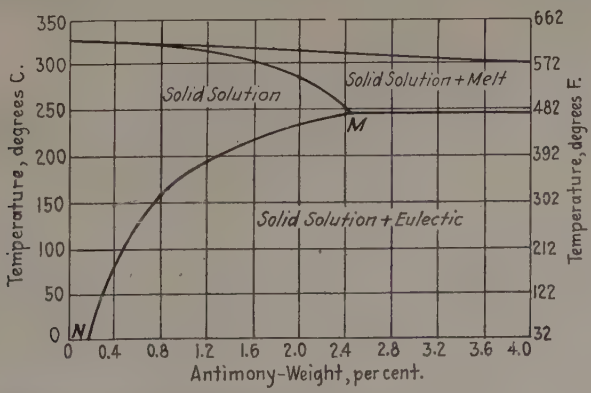

FIG. 7.—HIGH LEAD END OF ANTIMONY-LEAD DIAGRAM. (DEAN. REPRODUCED FROM A. S. S. T. HANDBOOK, 1929.)

is represented in Fig. 7. Two and one-half per cent. of antimony is soluble in lead at 248° C. The solubility at lower temperatures is indicated by the line *MN*.

The arsenic-antimony system[3] (Fig. 8) shows a complete miscibility of both solid and liquid. The system arsenic-lead[4] (Fig. 9) has a eutectic at 2.3 per cent. arsenic melting at 288° C., but no solid solubility is reported. The next step was, therefore, to determine whether there

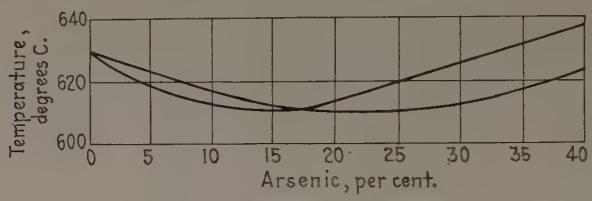

FIG. 8.—ARSENIC-ANTIMONY SYSTEM. (PARRAVANO AND DE CESARIS.)

might be any solid solubility of arsenic in lead which would be available for increased dispersion hardening of the alloy.

A series of lead-arsenic alloys were made containing up to 2.0 per cent. arsenic. The alloys were cast into cylindrical slugs (1¼ in. high

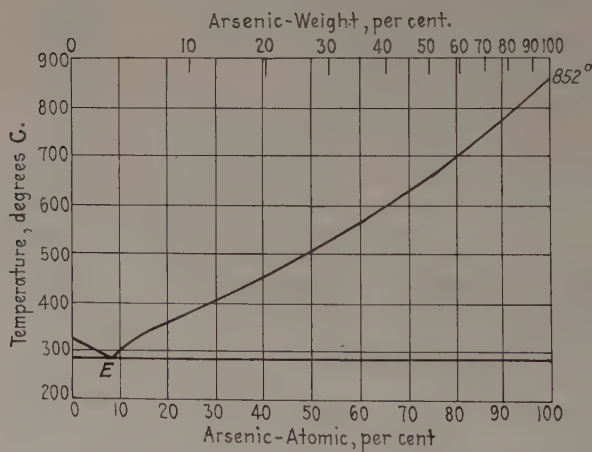

FIG. 9.—ARSENIC-LEAD SYSTEM. (HEIKE.)

by 1 in. dia.) and extruded to wires of 0.047 in. dia. The conductivity of these wires was measured at room temperature and at 100° C. by the ordinary potential drop method. From the results indicated in Table 4, it is evident that up to 100° C., there is no solid solubility of arsenic in lead.

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[3] Parravano and P. de Cesaris: Die Arsen-antimonlegierungen. *Intern. Ztsch. f. Metallog.* (1912) **2**, 70.

[4] Heike: Das Erstarrungs-diagramm der Blei-arsenlegierungen und der Schmelzpunkt des Arsens. *Intern. Ztsch. f. Metallog.* (1914) **6**, 49.

TABLE 4.—*Conductivity of Lead-arsenic Alloys in Mhos per Gram-meter*

As, Per Cent.	Conductivity at 25° C.	Conductivity at 100° C.
0.0	0.4157	0.3237
0.005	0.41507	0.32485
0.01	0.41512	0.32295
0.03	0.41492	0.32539
0.05	0.41495	0.32349
0.07	0.41497	0.32345
0.10	0.41451	0.32363
0.2	0.41102	0.32310
0.3	0.41079	0.32304
0.5	0.40975	0.32164
1.0	0.41031	0.32116
2.15	0.40788	0.31768

The wires were then annealed at 282° C., which is 6° below the eutectic temperature, and water-quenched. The tensile strength was measured immediately after quench and after aging at various temperatures. The results are presented in Table 5.

TABLE 5.—*Tensile Strength of Lead-arsenic Alloys in Kg. per Mm.*^{2} *after Heat Treatment at 282° C.*

As, Per Cent.	As Quenched	Aged at 144° C., 1 Hr.	Aged at 100° C., 18 Hr.	Aged at 50° C., 18 Hr.	Aged at 20° C., 25 Days
0.005	1.66	1.39	1.41	1.48	
0.01	1.87	1.55	1.67	1.60	
0.03	2.10	1.55	1.42	1.83	
0.05	2.37	1.60	1.92	1.98	
0.07	2.78	1.83	1.87	1.98	
0.10	2.46	1.73	1.53	2.08	2.35
0.20	2.64	1.78	1.64	2.09	2.34
0.30	2.64	1.90	1.68	2.00	2.47
0.50	2.56	1.76	1.56	1.92	2.37
1.00	2.85	2.11	2.11	2.34	2.37
2.00	2.69	2.37	2.25	2.55	2.82

It will be seen from the table that no regular increase of tensile strength takes place upon aging, and it may consequently be assumed, in view of the conductivity results at lower temperatures, that there is no solid solubility of arsenic in lead even at 280° C. Aging at elevated temperatures softens the alloys, probably due to agglomeration of the arsenic.

CONCLUSION

The effect of arsenic on dispersion-hardenable lead-antimony alloys can now be explained in the light of these experiments. The arsenic

has no solid solubility in lead and is known to form a continuous series of solid solutions with antimony. Therefore, immediately after annealing and quenching the antimony is in solid solution in the lead, and there is a certain amount of eutectic between the lead-antimony solid solution and arsenic. After quenching, the lead-antimony solid solution is supersaturated (the same as if arsenic were not present) and minute crystals of antimony separate. Since arsenic is soluble in antimony, some of the arsenic present will be concentrated in the surface layer of the minute antimony particles, which will then possess surface conditions different from those of pure antimony particles. The condition of the alloy at this stage is analogous to a suspension in a liquid which has been partly stabilized by a third constituent. Agglomeration and precipitation will occur, but at a much slower rate than if the third constituent were not present. Arsenic, therefore, is to be considered as a retardant for the agglomeration of minute antimony particles in the lead matrix. The length of the stabilization time decreases at elevated temperatures. The offered explanation is in agreement with the fact that the increase in hardness is practically independent of the percentage of arsenic within limits investigated. The addition of a third constituent insoluble in the solvent and forming a continuous series of solid solutions with the solute, might be of advantage to other kinds of age-hardenable binary alloys.

Acknowledgment

The author wishes to thank R. A. Morgen and Miss E. H. Roberts for making the conductivity measurements recorded and also for suggestions regarding the explanation offered for the effect of arsenic. The investigation was carried out under the direction of R. S. Dean.

A Metallographic Study of Tungsten Carbide Alloys

By J. L. Gregg* and C. W. Küttner,* Chicago, Ill.

(New York Meeting, February, 1929)

Recently there has been considerable interest in the production and use of extra hard alloys composed primarily of tungsten and carbon. Dr. Hoyt's recent paper[1] gives a good description of these alloys and describes their performance when used as tools. There are a number of these alloys on the market sold under various trade names, and it is the purpose of this paper to describe the results of an investigation of the structure of five of these alloys by means of microscopic and X-ray methods. The samples studied were in the form of small tools or wire-drawing dies, which were either purchased or supplied as samples. They were in some cases not supplied by the original makers but were furnished by the agents in this country, and we wish to call attention to the fact that they may not be truly representative of the materials supplied under the various trade names. No performance data are given and no inference as to the inferiority of one alloy as against any other is made.

K. Schröter[2] recently described methods for polishing alloys of this type for microscopic examination and has presented photomicrographs of several alloys. However, he did not identify their constituents or describe methods for their identification.

Constituents and Their Identification

As far back as 1915 attempts were made to utilize tungsten carbides commercially, but the great brittleness of these carbides made these first attempts unsuccessful. Later, successful dies were made by sintering the powdered carbides with small amounts of iron, nickel, or cobalt. Due to the high melting points of the tungsten carbides (2600° to 2800° C.), it is difficult to melt the carbides without volatilizing almost quantitatively the added element of the iron group. Inasmuch as the added metal does not exceed 20 per cent. and is usually present in much smaller amounts, some understanding of the tungsten-carbon equilibrium dia-

* Metallographic Laboratory, Western Electric Co., Inc.

[1] S. L. Hoyt: Tungsten Carbide—A New Tool Material. *Trans.* Am. Soc. Steel Treating (1928) **14**, 695.

[2] K. Schröter: Zur Technik metallographischen Untersuchung sehr harter Metallegierungen. *Ztsch. f. Metallkunde* (1928) **20**, Heft 1, 31.

gram is necessary for an interpretation of the structures found in the commercial alloys.

Summarizing the work of various investigators[3] the following information exists in regard to the tungsten-carbon system:

1. In the solid state tungsten holds very little or no carbon in solution.

2. According to more recent investigators, the compound W_3C mentioned by Ruff does not exist.

3. The compound W_2C was first described crystallographically by Westgren and Phragmén, who, however, believed it to be a solid solution the composition of which was near that given by the formula W_2C. They found it to be of the hexagonal close packed lattice with the constants $a = 2.986$, $c = 4.172$, $c/a = 1.578$. Later, work by Becker and Hölbling and by Becker led to the conclusion that this phase is a true compound, having the crystal structure of cadmium iodide with the constants $a = 2.99$Å, $c = 4.72$Å, $c/a = 1.573$. This compound is readily soluble in a cold 1:4 mixture of nitric and hydrofluoric acids (Ruff and Wunsch).

Becker has found that W_2C undergoes an allotropic change at 2400° C. The structure normal at room temperature is that just described and is called αW_2C by Becker to distinguish it from βW_2C normal at high temperatures. βW_2C gives a typical X-ray pattern and the transformation from one form into another is accompanied by a marked metallic noise.

4. The compound WC has been recognized by most of the investigators of the tungsten-carbon system. Westgren and Phragmén found it to have a simple hexagonal lattice with the constants $a = 2.94$Å, $c = 2.86$Å, $c/a = 0.973$. Chemically it may be distinguished from W_2C in that it is soluble in a mixture of HF and HNO_3 only when heated.

5. According to Ruff and Wunsch eutectics are found between W and W_2C and between W_2C and WC. The eutectic between W_2C and

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[3] H. Moissan: Recherches sur le tungsténe. *Compt. rend.* (1896) **123,** 13.

P. Williams: Sur la preparation et les propriétés d'un nouveau carbure de tungsténe. *Compt. rend.* (1898) **126,** 1722.

S. Hilpert and M. Ornstein: Über eine einfache Darstellung von Molybdän- und Wolfram-carbiden. *Berichte* (1913) **46,** 1669.

O. Ruff and R. Wunsch: Arbeiten im Gebeit hoher Temperaturen 111. Wolfram und Kohlenstoff. *Ztsch. anorg. Chem.* (1914) **82,** 292.

A. Hultgren: Metallographic Study of Tungsten Steels, 50. New York, John Wiley & Sons. 1920.

M. R. Andrews: Production and Characteristics of the Carbides of Tungsten. *Jnl. Phys. Chem.* (1923) **27,** 270.

Westgren and Phragmén: Röntgenanalyse der Systeme Wolfram-Kohlenstoff und Molybden-Kohlenstoff. *Ztsch. anorg. Chem.* (1926) **156,** 27.

K. Becker and R. Hölbling: Einige Eigenschaften des Wolframcarbides W_2C. *Ztsch. angew. Chem.* (1927) **40,** 512.

Franz Skaupy: Über der Carbide des Wolframs und ihre Anwedung. *Ztsch. f. Elektrochemie* (1927) **33,** 487.

K. Becker: Die Konstitution der Wolframcarbide. *Ztsch. f. Elektrochemie* (1928) **34,** 640.

WC was found by them to occur at about 3.5 per cent. carbon and to have a melting point of about 2580° C.

6. Little information as to possible transformations in the solid state exists. According to Guertler the formation of eutectoids best explains the structures observed.

The commercial tungsten-carbide alloys, according to the patent literature, are generally prepared by sintering the compacted tungsten carbide which has been mixed with a few per cent. of powdered cobalt, nickel, or iron. Inasmuch as the alloys are usually not melted and are cooled rapidly after heating, it is probable that equilibrium conditions are not reached.

The alloys investigated were as follows:

Alloy	Form	C, Per Cent.	W, Per Cent.	Co, Per Cent.	Fe, Per Cent.
Thoran	Tool	3.94	95.85	0	
Diamonite	Tool	3.91	95.65	0	
Elmarid	Die	5.9	83.0	4.5	0.4
Walramite	Die				
Widia	Die	5.68	87.40	6.10	

Due to the smallness of the samples available, the above results of chemical analyses are not of great accuracy.

In order to determine just what constituents were present in the alloys, X-ray spectrograms were taken of each alloy. These spectra were obtained with a General Electric X-ray diffraction apparatus[4] (powder method) using the $K\alpha$ radiation of molybdenum, the K_β being filtered out by means of zirconia sheets. Eastman intensifying screens and Agfa films were used with an exposure of from 24 to 48 hr. The diffraction patterns obtained are shown in Fig. 1, together with the patterns for W_2C and WC as calculated from the values obtained by Westgren and Phragmén and verified by Becker and Hölbling. The pattern for Widia was obtained from the powdered alloy and those of the other samples by reflection from polished surfaces.

The patterns indicate quite conclusively that Thoran, Diamonite, Elmarid and Walramite consist both of W_2C and WC, while Widia consists of WC with no W_2C or at least not enough to furnish a pattern on the film. No constituents other than these carbides are revealed in any of the alloys by these diffraction patterns. The relative intensity of the W_2C lines and the WC lines cannot be used as a measure of the amounts of these constituents present, because in polishing some of the constituents are left in relief and for this reason would diffract more than

[4] W. P. Davey: A New X-ray Diffraction Apparatus. *General Electric Review* (1922) **25**, 565.

their share of the X-ray beam. The lattice constants were not determined with sufficient accuracy to indicate whether or not the tungsten carbide lattices had been altered by dissolving other constituents, such as cobalt.

To summarize the results of the study by X-ray diffraction, it is indicated that W_2C and WC are the chief, if not the only, constituents present in these alloys and that little or no W_2C is present in Widia.

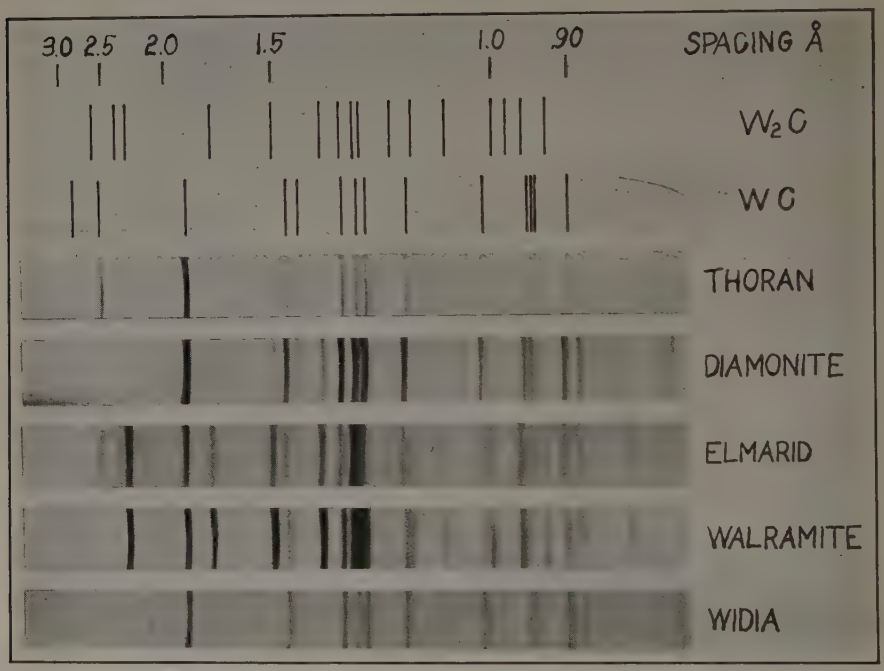

FIG. 1.—X-RAY DIFFRACTION PATTERNS OF ALLOYS INVESTIGATED.

PREPARATION OF SPECIMENS FOR MICROSCOPIC EXAMINATION

The samples were first ground on a medium coarse carborundum wheel, then with fine carborundum powder or emery flour on a bare metal wheel, next on the same bare metal wheel with levigated alumina and finally on a felt wheel with levigated alumina. This method of polishing takes about 2 hr. for a small sample when starting with the broken material. Schröter recommends the use of bort for polishing, but we did not find it much more satisfactory than the use of the materials outlined above.

MICROSTRUCTURE

The microstructures of Thoran and Diamonite are shown in Figs. 2 to 9. The black areas in these unetched alloys, as well as the other

alloys investigated, may be due either to porosity or to friable portions being inadvertently removed during polishing. For the pictures at high magnification, areas as free from holes as possible were selected. As these micrographs indicate both alloys consist of what appears to be an eutectic or eutectoid surrounded by a network which stands in relief

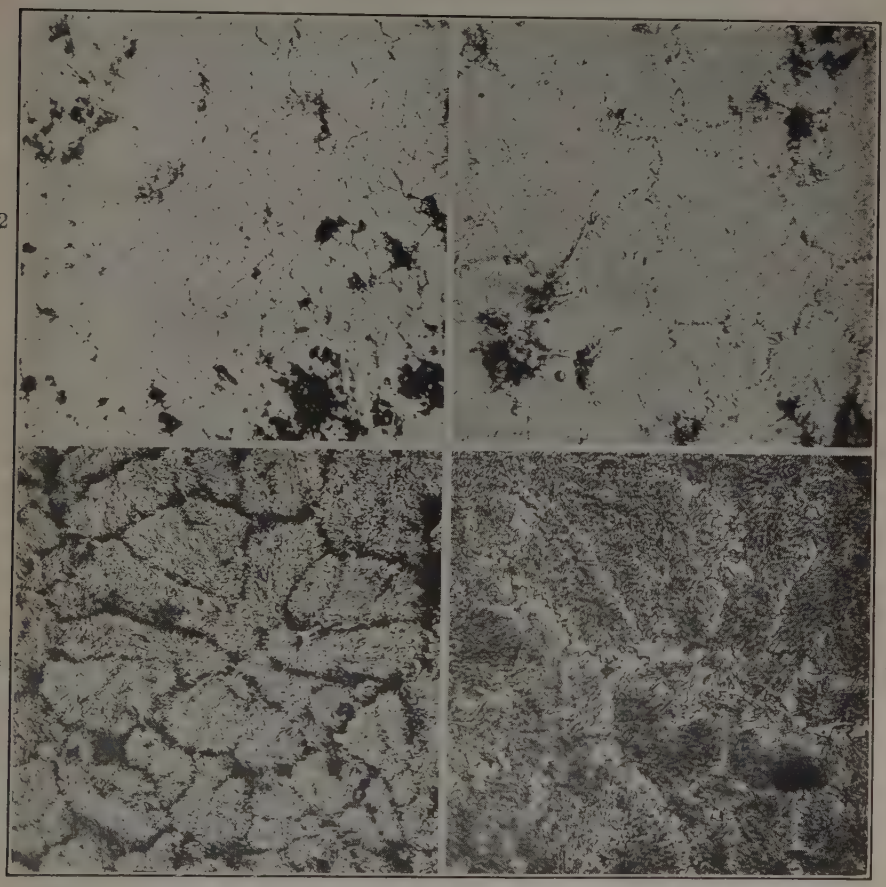

FIG. 2.—THORAN, UNETCHED. × 100.
FIG. 3.—THORAN, UNETCHED. × 400.
FIG. 4.—THORAN, ETCHED WITH $NaOH + K_3Fe(CN)_6$. × 400.
FIG. 5.—THORAN, ETCHED WITH $HF + HNO_3$. × 750.
(Reduced to approximately ⅔ original size.)

after polishing. Figs. 4 and 8 indicate that the network is attacked by alkaline ferricyanide, while Figs. 5 and 9 indicate that it is unattacked by a mixture of nitric and hydrofluoric acids. Work of other investigators[5] has indicated that W_2C is soluble in a mixture of nitric and hydrofluoric acids, while WC is not unless the acids are heated. This would indicate

[5] See footnote No. 3.

that the network is WC, which hypothesis is substantiated by an X-ray study which we will now describe.

Two samples of Thoran were prepared as for microscopic examination; the sample lettered *A* was given a prolonged etch with alkaline ferricyanide, and the sample lettered *B* was given a deep etch with the

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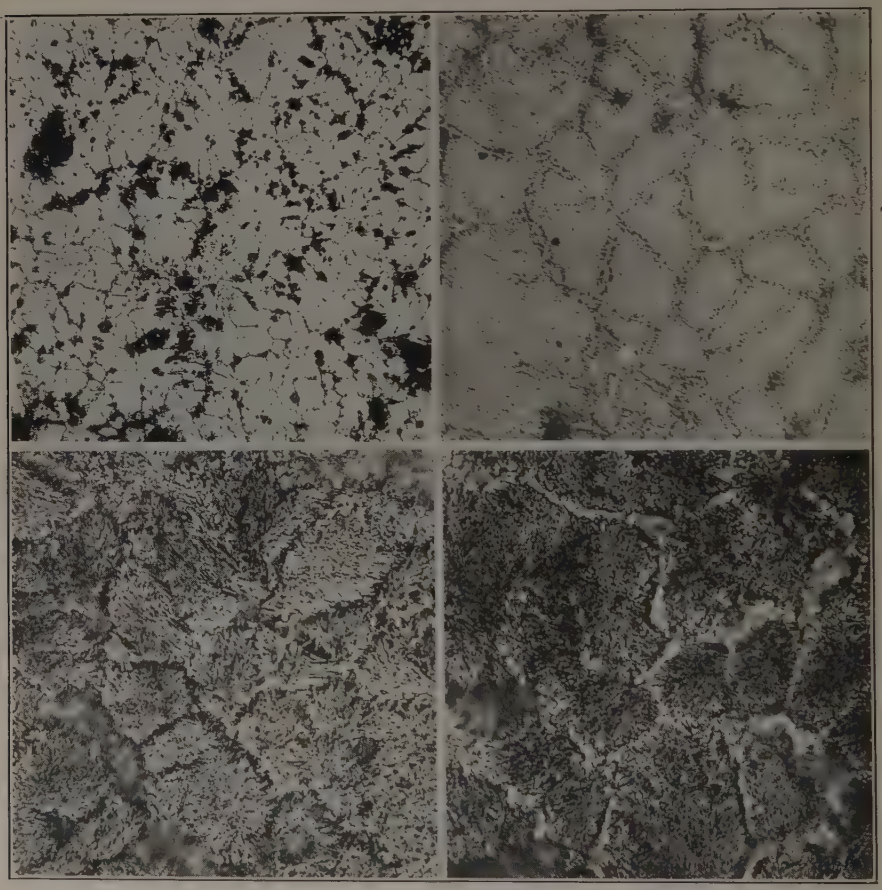

FIG. 6.—DIAMONITE, UNETCHED. × 100.
FIG. 7.—DIAMONITE, UNETCHED. × 400.
FIG. 8.—DIAMONITE, ETCHED WITH $NaOH + K_3Fe(CN)_6$. × 750.
FIG. 9.—DIAMONITE, ETCHED WITH $HF + HNO_3$. × 750.
(Reduced to approximately ⅔ original size.)

mixture of nitric and hydrofluoric acids. The two samples were then placed in the same cassette of the General Electric X-ray spectrometer previously mentioned and spectra obtained by reflection of the primary beam from the etched surfaces. As the spectrograms shown in Fig. 10 indicate, both the WC and W_2C lattices are indicated by sample *A*, while sample *B* appears to be composed only of WC. A relatively small depth of

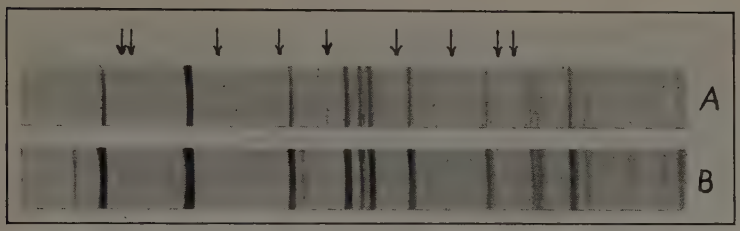

FIG. 10.—X-RAY PATTERNS BY REFLECTION FROM ETCHED THORAN. *A* etched with NaOH + $K_3Fe(CN)_6$. *B* etched with HF + HNO_3. Arrows indicate W_2C lines present in *A* and absent in *B*.

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13 14

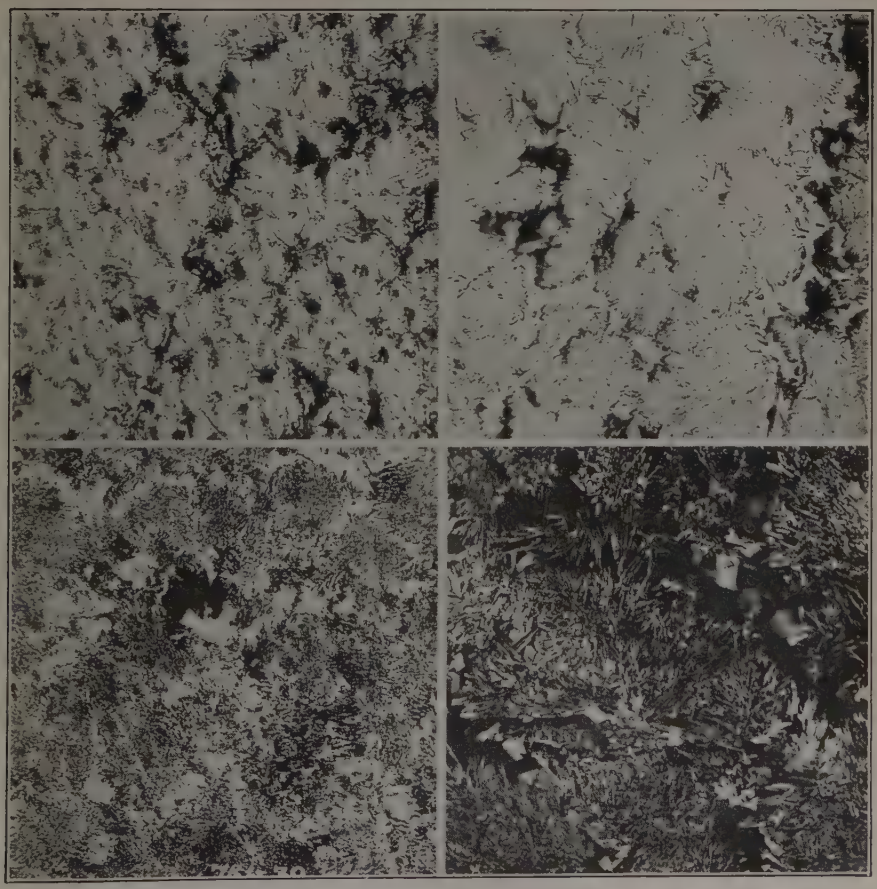

FIG. 11.—ELMARID, UNETCHED. × 100.
FIG. 12.—ELMARID, UNETCHED. × 400.
FIG. 13.—ELMARID, ETCHED WITH NaOH + $K_3Fe(CN)_6$. × 400.
FIG. 14.—ELMARID, ETCHED WITH HF + HNO_3. × 750.
(Reduced to approximately ⅔ original size.)

etching is sufficient for this experiment because the penetration of the X-rays in a metal of high atomic weight is very small. Inasmuch as this alloy is composed mostly, if not entirely, of W_2C and WC, it is evident that the W_2C is dissolved by a mixture of nitric and hydrofluoric acids, while WC is unattacked, and that WC is darkened by alkaline

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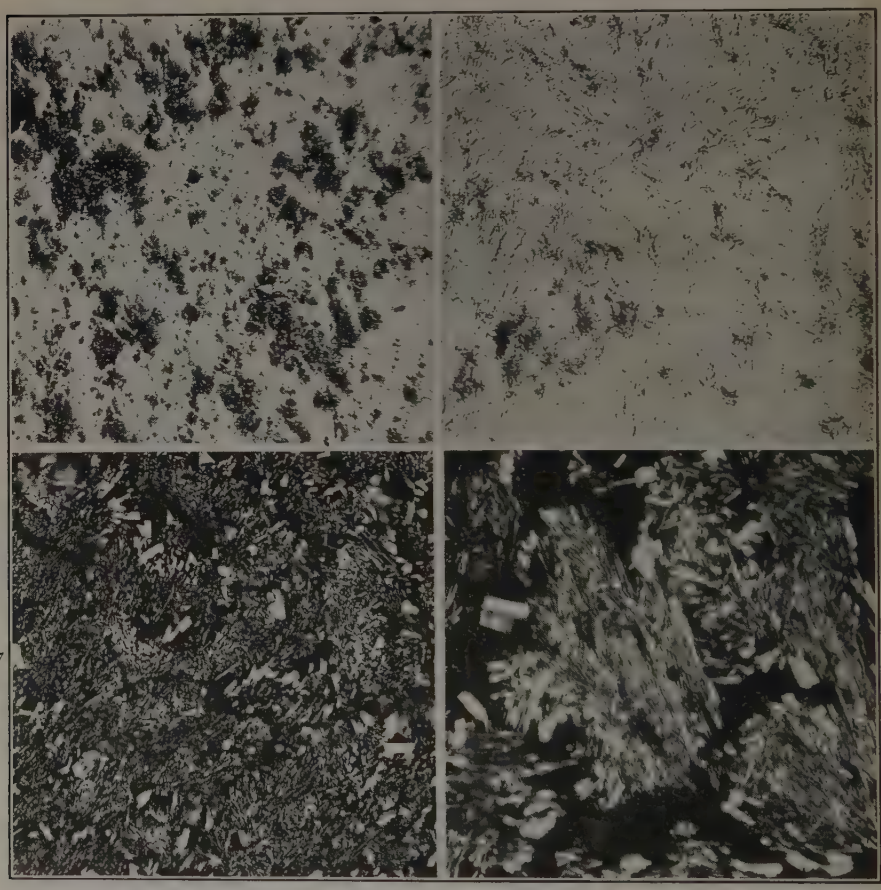

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FIG. 15.—WALRAMITE, UNETCHED. × 100
FIG. 16.—WALRAMITE, UNETCHED. × 400.
FIG. 17.—WALRAMITE, ETCHED WITH $HF + HNO_3$. × 750.
FIG. 18.—WALRAMITE, ETCHED WITH $NaOH + K_3Fe(CN)_6$. × 2000.
(Reduced to approximately ⅔ original size.)

ferricyanide while W_2C is unattacked. We thus have two very useful selective etching reagents for tungsten carbide alloys.

Both Thoran and Diamonite consist of a network of WC surrounding what appears to be an eutectoid or eutectic between W_2C and WC. No significant difference was observed between the microstructure of the two alloys.

The microstructure of Elmarid is shown in Figs. 11 to 14 and Fig. 22. Its structure is somewhat similar to that of Thoran and Diamonite in that it consists of what might well be an eutectic surrounded by a network. The network, however, appears to consist partly of W_2C and

19 20

21 22

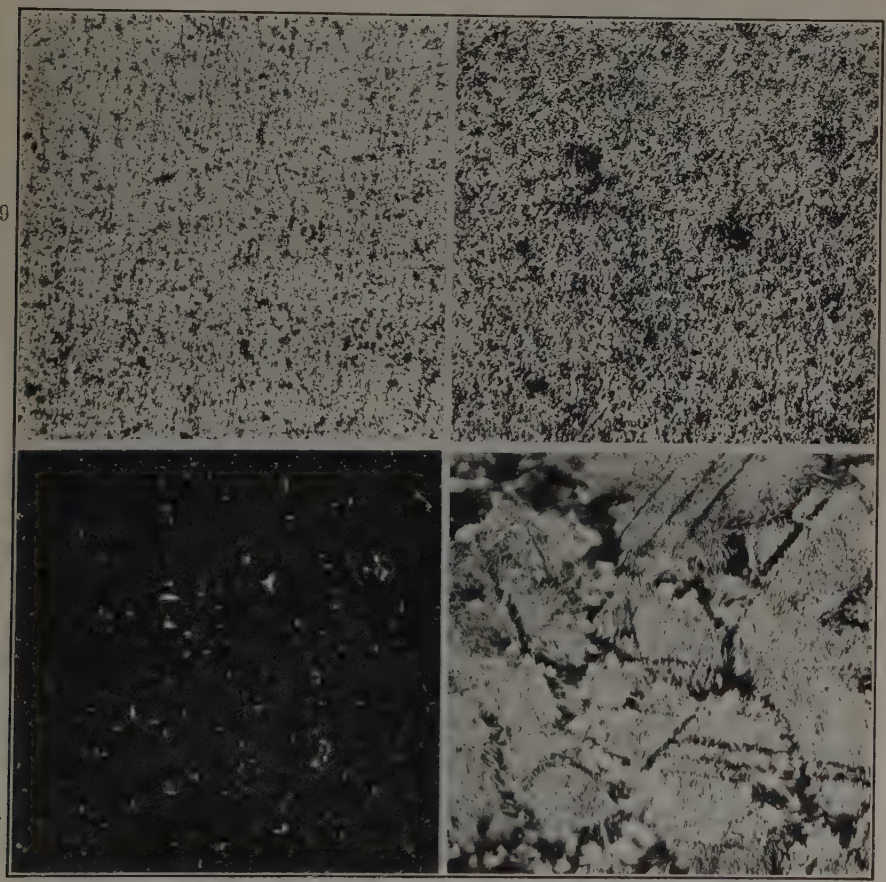

FIG. 19.—WIDIA, UNETCHED. × 100.
FIG. 20.—WIDIA, UNETCHED. × 400.
FIG. 21.—WIDIA, ETCHED WITH $NaOH + K_3Fe(CN)_6$. × 750.
FIG. 22.—ELMARID, ETCHED WITH SODIUM PICRATE FOLLOWED BY $HF + HNO_3$. × 400.

(Reduced to approximately ⅔ original size.)

partly of WC. The WC not in the network is located along crystallographic planes in such a manner as to give the appearance of a Widmanstättian structure as shown in Fig. 22.

The structure of Walramite as shown in Figs. 15 to 18 is similar to Elmarid in that there is a heterogeneous network surrounding what has the appearance of an eutectic. The structure of the matrix is much

finer than that in Elmarid and as may be seen from the unetched samples, there does not appear to be as much difference in hardness between the network and matrix in Walramite as there is in Elmarid.

Figs. 19 to 21 are of Widia. As was shown in Fig. 1, Widia contains only WC in sufficient quantities to be detected from a powder picture. Etching tests also indicate that no W_2C is present as the sample was wholly unattacked by the mixture of nitric and hydrofluoric acids. The structure of the alloy has been very poorly revealed and it is just possible to hazard the guess that it consists of fine grains of WC bound together with some unknown constituent.

Summary

Five different commercial tungsten carbide alloys were investigated by means of X-ray diffraction patterns and microscopic examination. Both W_2C and WC were found in four alloys and only WC in the fifth alloy. The behavior of two selective etching reagents is described; alkaline ferricyanide attacks WC and not W_2C; a mixture of concentrated nitric and hydrofluoric acids attacks W_2C and not WC. The structure of the alloys containing both W_2C and WC resembles that of an eutectoid surrounded by a network of WC or a complex network.

DISCUSSION

S. L. Hoyt, Schenectady, N. Y.—The authors have given us a very interesting paper, describing X-ray analysis and etching methods for identifying the constituents of tungsten carbide alloys. I have tested out these same methods and believe that what they say is sound. The photographs of Widia indicate that it is a sintered material while the rest are undoubtedly cast materials. The sintered material does not show the eutectic structure.

The authors have used aluminum powder for polishing these carbides, and while they state that the method is satisfactory, I think that it can be improved upon, and in my own work on similar materials I have found that the coarse grinding on the carborundum wheel can very satisfactorily be followed by a boron carbide lap, using powder of approximately 150 to 200 mesh. Boron carbide is much harder than alumina and by proper handling on the lapping disk it can be made to cut down the surface fairly rapidly and to produce a reasonably good polish. Its principal feature here is that it leaves the surface in good shape for polishing subsequently with diamond dust.

The boron carbide lap can be followed by a fine diamond dust, which produces a bright polish in a comparatively short time. This work is done on an ordinary wooden lap, using almond oil. Both the boron carbide and diamond dust are so fast and so excellent in their behavior that microsections of these materials can be prepared in a reasonably short time—I believe in much shorter time than is given by the authors.

We have taken photographs of these materials at 1000 dia., some of them at 5000 dia., and judging from the photographs I believe the technique which I have described is entirely satisfactory.

Grain Growth in Metals Caused by Diffusion

Discussion of paper by Floyd C. Kelley (*Proc.* Inst. of Met. Div., 1928, page 390.)

A. Hultgren, Söderfors, Sweden (written discussion*).—From the results obtained in his own experiments as well as those of Austin and of Grube Mr. Kelley derives a general law, expressed tentatively in the following words: "whenever two metals are brought into intimate contact at a temperature at which diffusion takes place, a comparatively rapid, or abnormal, grain growth results."

It is suggested that, in order adequately to represent the facts, this definition should be restricted by the following qualifications: a and b are the two metals, b diffusing into a.

A. At the temperature in question a should exist as phase a_1 having a limited solubility for b.

B. The supply of b by diffusion should be sufficient, in view of the rate of diffusion into a_1, to increase the concentration of b above the saturation value in a_1 so as to cause a new phase a_2 to form.

C. The phase a_2 should have a range of solubility for b, thus rendering continued diffusion possible.

D. In order that the columnar grains may be preserved in the structure the phase a_2 should, of course, not suffer transformation on cooling.

The phenomenon thus defined may be described as *progressive transformation by diffusion*. Its mechanism would appear to be as follows:

Fig. 17 shows a portion of the equilibrium diagram a-b, Fig. 18 the distribution of b in solution after various periods of diffusion, Fig. 19 represents the structure in cross-section of a cylindrical rod of a at the end of heating period 3.

1. The first effect of diffusion of b into a will be to establish a concentration gradient in phase a_1 (1, Fig. 18). When the saturation value for the temperature of the experiment (m, Fig. 17) is reached at the surface, nuclei of a_2 of composition n will form here, and later develop into a continuous layer. Assuming that diffusion proceeds without irregularities and that transformation at any point sets in without lag—*i. e.*, in the moment saturation is exceeded—the transformation a_1-a_2 will advance inwards on a cylindrical surface concentric with the surface of the rod. The discontinuity of composition at the transformation surface in the position it happens to have at the end of the treatment (3, Fig. 18) will be preserved at room temperature, if the cooling is not particularly slow, and be recorded in the structure as a marked, smooth line, in agreement with Grube's and the author's observations. The shape of the distribution curves in Fig. 18 is also corroborated by the analyses given by Grube.

2. During diffusion, since the secondary phase a_2 is always in immediate contact with the saturated part of the primary phase a_1, there should be very little lag in the transformation. This means that the first a_2 grains formed should grow in preference to the formation of independent nuclei; in other words, columnar growth results. It does not seem necessary to assume, with Green,[1] whose conception of the phenomenon

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* This discussion was written in April, 1928, but was lost in transit. The second copy reached the Institute too late for inclusion in the 1928 volume.

[1] Discussion of Austin's paper: Hydrogen Decarburisation of Carbon Steels with Consideration of Related Phenomena. *Jnl.* Iron and Steel Inst. (1922) **105,** 147.

otherwise is very similar to the writer's, that particles of a_2 formed in transformation are immediately absorbed by the previously formed grains. In that case recrystallization would be involved.

3. Diffusion velocity may be a function of crystallographic direction. If it be assumed that the first nuclei of a_2 have a random orientation of their crystal axes, it would follow that grains having a direction of fast diffusion coinciding with the direction of the steepest concentration gradient, *i. e.*, with the radial direction, would grow faster than their neighbor grains and have an opportunity of spreading at the front, so as to inclose the latter grains and stop their growth.

4. Rate of transformation, regardless of diffusion and concentration gradient, may be a function of crystallographic direction in the a_2 grains. Assuming a certain

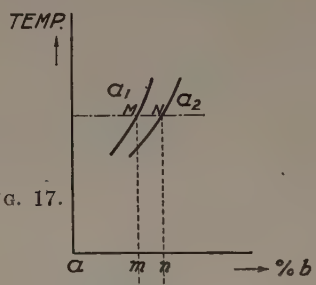

Fig. 17.

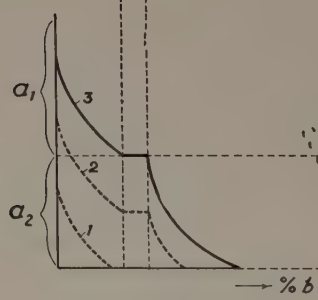

Fig. 18.

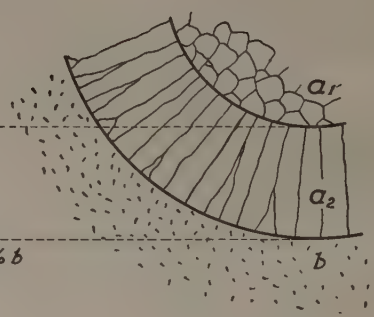

Fig. 19.

lag, this would also result in the favored grains growing faster than the others. For either of the reasons mentioned in paragraphs 3 and 4, the columnar grains would become fewer and broader as they grow inwards. Whatever the reason, this feature is very clearly brought out in the author's Figs. 1 and 2. The columnar structure as such, however, is no proof of vectorial properties in the a_2 crystal grain, but simply a consequence of the fact that the direction of fastest diffusion is perpendicular to the surface, in combination with the absence of independent nuclei.

5. If a contains a third element c that forms solid solutions with a_1 and a_2, the concentration of c in the two phases would be different; say, higher in a_1. Thus the transformation would be retarded by accumulation of c in a_1 in a zone ahead of the a_2-a_1 surface, and, furthermore, independent nuclei of a_2 might form at the front of

that zone. Therefore purity would be expected to favor progressive transformation by diffusion.

6. On cooling after the diffusion experiment, if the equilibrium diagram is of the type shown in Fig. 17, the transformation will first advance gradually to points of lower concentration, the whole mass finally being converted into a_2. The columnar growth will probably continue during the first part of the cooling, owing to the concentration gradient, to a depth dependent on the rate of cooling. This explains why most of the columnar grains extend across the line of discontinuity.

7. Mr. Kelley reports that some of those grains show no discontinuity after etching. This is probably due to their being sectioned in a crystal plane of equal attack by the etching reagent in the portions of high and low concentration, perhaps a plane of a certain indifference against etching (see the author's Figs. 3, 4 and 8).

8. In the systems iron with chromium, tungsten, molybdenum, aluminum, silicon and tin—all probably of the type shown in Fig. 20—diffusion at a temperature between A_4 and A_3 will cause columnar growth of α (δ) iron as a result of progressive transformation from γ iron. The experiments of Grube and of the author verify this conclusion. If the temperature of diffusion (t, Fig. 20) is in the upper range, subsequent cooling will cause the transformation surface $\gamma \rightarrow \alpha$ (δ) first to retreat to a position of higher concentration and then to advance again following the loop in the diagram. If the cooling is not too rapid a record of the retreat may be left in the form of a second line of discontinuity in the structure. Fluctuation of temperature during treatment might have a similar effect (see Mr. Kelley's Fig. 8).

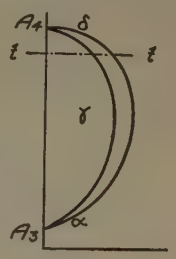

Fig. 20.

9. If, in a system of the type mentioned in paragraph 8, diffusion takes place above A_4 or below A_3 (Fig. 20), it is not accompanied by transformation or columnar growth. In the former case, however, columnar grains might form in cooling, owing to the concentration gradient established, in a limited zone that passes the double transformation $\delta \rightarrow \gamma \rightarrow \alpha$.

10. Both nickel, manganese and carbon raise A_4 and lower A_3 in iron. Diffusion of those elements into iron at temperatures between A_4 and A_3 cannot therefore cause the γ iron to transform into α iron. In the case of nickel diffusing into γ iron columnar growth is entirely excluded since those two metals form a continuous series of solid solution.

11. Such is not the case with manganese and γ iron, however. Therefore, as shown in the author's Fig. 7, a new phase may form on diffusion at the surface of the iron. The large crystals shown may consist of deposited manganese or a high-manganese constituent formed by reaction between iron and manganese vapor or perhaps molten manganese. The serrated outer contour appears to indicate outward growth.

12. The system iron-carbon is peculiar. When carbon diffuses into iron a second phase, cementite, may appear. To the writer's knowledge columnar grains of cementite formed by carburization of iron have not been observed, probably because conditions 3 and usually 2 are not fulfilled. If δ iron, between the peritectic and A_4, or α iron between A_3 and A_1, is carburized, the secondary phase γ iron is formed, only to be transformed during cooling, thus condition 4 is not satisfied.

13. By *removal* of carbon, however, by diffusion, between A_3 and A_1, from austenite, or γ iron with carbon in solution, columnar growth of α iron through progressive transformation may be observed, as shown in the decarburization experiments by Austin and by the author and undoubtedly noticed many times in metallographic laboratories where the structure of steel annealed under decarburizing conditions has been inspected. Incidentally, the solubility of carbon, or possibly carbonaceous gases, in α iron is thereby proved. Columnar crystallization of α iron by decarburization

of steel is exactly the same general phenomenon as the one defined by conditions 1 to 4, and in order to be covered by those conditions, it is only required to alter the wording into terms of removal by diffusion and decrease in concentration.

14. Analogous cases of columnar growth of α or δ iron by decarburization of austenite have been noticed by Kalling[2] in 14 per cent. chromium steel (about 1000° C.) and by the writer in high-speed steel (about 1300° C.). Such observations are of interest in showing that purity, or freedom from a third element, dissolved in the primary phase, is not essential in columnar growth as a result of progressive transformation by diffusion.

15. Stead and Carpenter[3] observed coarse columnar crystallization in strips of electrolytic iron that had been heated somewhere above A_3. It was demonstrated that the experiment was successful only if the iron was pure and the strip not too thick. This may be explained by assuming that, owing to the thinness of the strip, a suitable *temperature gradient* was established and existed during the Ar_3 transformation. The latter was, of course, brought about by cooling; *i. e.*, by *diffusion of heat* in the direction of the gradient. Thus, here is also an instance of columnar growth as a result of transformation by diffusion, only the latter term being taken in a wider sense. Transformation in this case was, of course, rapid, and impurities, if such had been present, would therefore probably have retarded it sufficiently to enable independent nuclei of α iron to form.

16. A reference to the columnar growth of crystals in ingots may not be out of place. Although this phenomenon presents certain peculiar features, the general principles of transformation by diffusion (of heat) through a moving gradient (of temperature) apply here also.

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[2] B. Kalling and G. Pagels: Microstructure and Properties of High-chrome Steel. *Jernkont. Ann.* (1926) **81,** 209.

[3] J. E. Stead and H. C. H. Carpenter: Crystallising Properties of Electro-deposited Iron. *Jnl.* Iron and Steel Inst. (1913) **88,** 119.

INDEX

(NOTE: In this index the name of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the titles of papers in *italics*.)

A

Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon (ELLIS) 443; *Discussion*, 468
Acid-resistant alloys, 149, 160, 248
ACKERMAN, D. E.: *Discussions: on Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids*, 171
on Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids, 279
ACKERMAN, D. E. AND PILLING, N. B.: *Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids*, 248
Aircraft: casting alloys, aluminum and magnesium, stability, 333
Alclad 17ST, diffusion of core and coating, 555
Alloys, acid-resistant, 149, 160, 248
Aluminum: Corrosion. *See* Corrosion of Metals.
diffusion of pure aluminum and alloy, 555
films, stripping from surface, 13
Aluminum alloys: stability of casting alloys, 333
Aluminum-magnesium alloys: equilibrium relations in alloys of high purity, 351
review of work on constitution of system, 351
A. I. M. E.: Divisions: Institute of Metals, officers and committees, 5
officers and directors, 5
ANDERSON, E. A.: *Discussion on Stability of Aluminum and Magnesium Casting Alloys*, 350
ANDERSON, E. A. AND PEIRCE, W. M.: *Some Practical Aspects of Creep in Zinc*, 560
ARCHER, R. S.: *Discussion on Stability of Aluminum and Magnesium Casting Alloys*, 347
Arsenic: effect on dispersion-hardenable lead-antimony alloys, 573

B

BEDWORTH, H. A.: *Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids*, 160; *Discussion*, 174
BENGOUGH, G. D., STUART, J. M. AND LEE, A. R.: *Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions*, 29
BOECK, J. W.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 492
BOLTON, J. W.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 495
BOLTON, J. W. AND WEIGAND, S. A.: *Incipient Shrinkage in Some Non-ferrous Alloys*, 475
Brass (*See also* Copper-zinc Alloys):
etching and smoothing, by hand methods, 295
high-strength, bibliography, 528
causes, 508
properties, 508
nickel-silicon: heat treatment effect on mechanical properties, 536
sheet: fatigue endurance and related properties, 549
strengthening, effect of tin, 510, 531
effect of various elements, 508, 515
60:40 (*See* Muntz Metal).
Brass scrap: testing before buying, 492
Britannia metal: bibliography, 379
differs from pewter, 373
physical properties, effect of cold rolling and heat treatment, 373
Bronze (*See also* Copper-zinc Alloys):
etching and smoothing, by hand methods, 295
phosphor: heat treatment effect on mechanical properties, 546
Bronze castings: porosity, causes, 479
shrinkage, incipient, 475

C

CAPILLON, E. A.: *Discussion on High-strength Gold Alloys for Jewelry*, 406
CARTER, F. E.: *Discussions: on High-strength Gold Alloys for Jewelry*, 406
on Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal, 383
Casting copper: absorbability of gases and effect of adding cuprosilicon, 443
gases in overpoled, fire-refined sample, 470
CHURCHILL, H. V.: *Inhibition of Corrosion of Aluminum by Soaps*, 244
CLARK, F. H.: *Discussions: on Diffusion of Zinc into Copper*, 556
on High-strength Brasses, 533
on Smoothing and Etching Cupronickel, Bronze, Brass and Steel, 308
on Some Observations in Heat Treatment of Muntz Metal, 507

Cold rolling: effect on physical properties of Britannia metal, 373
Constitution of the Copper-silicon System (SMITH) 414; *Discussion*, 440
Copper: casting, absorbability of gases and effect of adding cuprosilicon, 443
diffusion of zinc into, rate and temperature, 552
films, stripping from surface, 13
overpoled, fire-refined, gases in, 470
Copper alloys (*See also* Bronze and Brass): dispersion hardening, cause and effect, 409
Copper auride, evidence of existence, 405
Copper-silicon alloys: anode used at Chuquicamata, 440
constitution, 414
equilibrium diagrams, 414
Copper-silicon-manganese alloys: acid-resistant, 160
corrosion. *See* Corrosion of Metals.
Copper-tin alloys: heat treatment effect on mechanical properties of those containing nickel and silicon, 535
Copper-zinc alloys: heat treatment effect on mechanical properties of those containing nickel and silicon, 535
Correlation of Laboratory Corrosion Tests with Service: Weather-exposure Tests of Sheet Duralumin (RAWDON) 220; *Discussion*, 241
Corrosion-fatigue: constant-damage graphs and surfaces, 56
corrosion-stress relation to fatigue limit, 56
definition, 56
effect of pitting vs. that of absorbed hydrogen, 47
endurance limit, definition, 56
prior-corrosion fatigue, definition, 56
stress-time-cycle relations, 56
Corrosion of metals: acid-resistant alloys, 149, 160, 248
aluminum, inhibiting effect of soap, 244
as affected by stress, time, and number of cycles, 56
copper-silicon-manganese alloys, acid-resistant, 160
Corrosion-fatigue. *See* Corrosion-fatigue.
duralumin: nature of structural change, 221
weather-exposure tests, 220
effect of passivity, 7
effect on human body when taken in food, 181
effect on milk, 217
in water and salt solutions, quantitative measurements, 29
iron: relation of passivity, 7
rust, causes, 26
definition, 21
effect on further corrosion, 27
prevention, 26
iron-nickel-chrominum alloys, resistance to acids, 248
laboratory tests, value, 220
measurement by weight loss insufficient, 288
milk as corrosive medium, 177
monel metal, resistance in milk, 175
Corrosion of metals: nickel, resistance in milk, 175
periodicity of solution, 279
"pilot" tests, 220
protective films, 7, 238, 242
steel, relation of passivity, 7, 23
testing methods contrasted, 171, 175, 242
tin alloys, 140
tin and its alloys, 111
tin, corn or can black, 133, 147
tin pest, 114
tin plate by food products, 132
weathering tests, duralumin, 220
weathering tests in Lehigh Valley, Pa., 280
weathering tests in various parts of United States, 287
zinc, in water and salt solutions, quantitative measurement, 33
Corrosion of Metals as Affected by Stress, Time, and Number of Cycles (MCADAM) 56; *Discussion*, 53
Corrosion of Metals in the Lehigh Valley (REINHARD) 280; *Discussion*, 288
Corrosion of Tin and Its Alloys (MANTELL) 111; *Discussion*, 146
Corrosion-stress. *See* Corrosion-fatigue.
CORSON, M. G.: copper-silicon diagram, 416, 437, 439, 440
Discussions: on Constitution of the Copper-silicon System, 440
on Equilibrium Relations in Aluminum-magnesium Alloys of High Purity, 366
on Incipient Shrinkage in Some Non-ferrous Alloys, 493
on High-strength Brasses, 532
Cupronickel: etching and smoothing by hand methods, 291
Cuprosilicon: effect of adding to casting copper, 443

D

DALBEY, C. E.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 492
DALZELL, R. C.: *Discussion on Gases in a Sample of Overpoled Fire-refined Copper*, 474
DEAN, R. S.: *Discussion on Absorbability of Gases in Casting Copper*, 468
Diamonite, metallographic study, 583
Diffusion of metals: aluminum alloy into pure aluminum, 555
effect on grain growth, 591
steps in process, 558
zinc into copper, 552
Diffusion of Zinc into Copper (HOYT) 552; *Discussion*, 555
Dispersion Hardening in Copper-base and Silver-base Alloys (GREGG) 409
Dispersion hardening: in copper and silver alloys, 409
in nickel-silicon brass and bronze, 547
DIX, E. H. JR.: *Discussion on Correlation of Laboratory Corrosion Tests with Service: Weather-exposure Tests of Sheet Duralumin*, 241

DIX, E. H. JR. AND KELLER, F.: *Equilibrium Relations in Aluminum-magnesium Alloys of High Purity*, 351; *Discussion*, 369
Duralumin: corrosion. *See* Corrosion of Metals.
weather exposure tests, 220

E

Effect of Arsenic on Dispersion-hardenable Lead-antimony Alloys (SELJESATER) 573
Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal (EGEBERG AND SMITH) 373; *Discussion*, 380
EGEBERG, B.: *Discussion on Effect on Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal*, 382, 383
EGEBERG, B. AND SMITH, H. B.: *Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal*, 373; *Discussion*, 383
ELDRIDGE, C. H.: *Discussion on Constitution of the Copper-silicon System*, 440
ELLIS, O. W.: *Absorbability of Gases in Casting Copper and Effect of Adding Cupro-silicon*, 443; *Discussion*, 468, 469
Gases in a Sample of Overpoled Fire-refined Copper, 470; *Discussion*, 474
High-strength Brasses, 508; *Discussion*, 533
Discussions: on Diffusion of Zinc into Copper, 556
on Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal, 380
on High-strength Gold Alloys for Jewelry, 405
ELLIS, W. C. AND SCHUMACHER, E. E.: *Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys Containing Nickel and Silicon*, 535; *Discussion*, 550
Elmarid, metallographic study, 583
Equilibrium Relations in Aluminum-magnesium Alloys of High Purity (DIX AND KELLER) 351; *Discussion*, 366
Etching cupronickel, bronze, brass and steel, by hand methods, 291
Etching reagent: chloric acid, limitations, 303
chromic acid, advantages for nickel and copper alloys, 291
for gold and silver alloys, 403, 405
EVANS, U. R.: *Passivity of Metals, and Its Relation to Problems of Corrosion*, 7
Discussions: on Corrosion of Tin and Its Alloys, 146
on Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids, 278
photograph, 6

F

FAWCETT, L. H.: *Discussion on High-strength Brasses*, 532
FIELD, B. E.: *Some New Developments in Acid-resistant Alloys*, 149; *Discussion*, 159
Films, stripping from metallic surfaces, 12
FINK, C. G.: *Discussions: on Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk*, 219
on Resistance of Copper-rich Copper-silicon manganese Alloys to Corrosion by Acids, 173, 174
FINKELDEY, W. H.: *Discussion on Corrosion of Metals in the Lehigh Valley*, 289
FRASER, O. B. J., *Discussion on Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk*, 219
FRASER, O. B. J., MCKAY, R. J. AND SEARLE, H. E.: *Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk*, 175
FULLER, T. S.: *Some Aspects of Corrosion-fatigue*, 47; *Discussion*, 55
Discussion on Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys, 549

G

GANN, J. A.: *Treatment and Structure of Magnesium Alloys*, 309
Discussion on Stability of Aluminum and Magnesium Casting Alloys, 350
Gases in a Sample of Overpoled Fire-refined Copper (ELLIS) 470; *Discussion*, 474
Gold alloys: age-hardening phenomena, 384
copper auride, evidence of existence, 405
etching reagent, 403, 405
high-strength, for jewelry, requirements and properties, 384
Gold-copper alloys: evidence of existence of Au Cu, 405
GRAHAM, W. F.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 491
Grain Growth in Metals Caused by Diffusion (KELLEY). *Discussion*, 591
GREGG, J. L.: *Dispersion Hardening in Copper-base and Silver-base Alloys*, 409
GREGG, J. L. AND KÜTTNER, C. W.: *Metallographic Study of Tungsten Carbide Alloys*, 581

H

HANSON, D. AND GAYLER, M. L. V.: diagram of Al-Mg alloys, 353
Hardening. *See* Dispersion Hardening.
Hardness: Brinell and scleroscope results contrasted, 375, 381
Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys Containing Nickel and Silicon (ELLIS AND SCHUMACHER) 535; *Discussion*, 549
Heat treatment: Britannia metal, effect on physical properties, 373

Heat treatment: copper alloys, effect on mechanical properties, 535
magnesium alloys, binary, effect on structure and properties, 309
Muntz metal, effect on cleavage structure, 498
precious-metal alloys, effect on, 406
High-strength Brasses (Ellis) 508; *Discussion*, 530
High-strength Gold Alloys for Jewelry and Age-hardening Phenomena in Gold Alloys (Wise) 384; *Discussion*, 403
Hippensteel, C. L.: *Discussion on Corrosion of Metals in the Lehigh Valley*, 289
Hoyt, S. L.: *Diffusion of Zinc into Copper*, 552; *Discussion*, 557, 558
Discussions: on Absorbability of Gases in Casting Copper, 468
on Metallographic Study of Tungsten Carbide Alloys, 590
Hultgren, A.: *Discussion on Grain Growth in Metals Caused by Diffusion*, 591

I

Incipient Shrinkage in Some Non-ferrous Alloys (Bolton and Weigand) 475; *Discussion*, 491
Inhibition of Corrosion of Aluminum by Soaps (Churchill) 244; *Discussion*, 247
Institute of Metals Division, officers and committees, 5
Iron: corrosion. *See* Corrosion of Metals.
films, protective, 7
films, stripping from surface, 12, 13
passivity, causes, 7, 14
rust. *See* Corrosion of Metals.
temper colors, 7
Iron-nickel-chromium alloys: acid resistance, 248
corrosion. *See* Corrosion of Metals.

J

Jeffries, Z: *Discussion on Diffusion of Zinc into Copper*, 556
Jewelry: gold alloys, high-strength, requirements and properties, 384
Johnson elastic limit in soft metals, 565

K

Keeley, R. J.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 495
Keller, F.: *Discussions: on Diffusion of Zinc into Copper*, 555
on Equilibrium Relations in Aluminum-magnesium Alloys of High Purity, 369
Keller, F. and Dix, E. H. Jr.: *Equilibrium Relations in Aluminum-magnesium Alloys of High Purity*, 351; *Discussion*, 369
Küttner, C. W. and Gregg, J. L.: *Metallographic Study of Tungsten Carbide Alloys*, 581

L

Leach, R. H.: *Discussion on High-strength Gold Alloys for Jewelry*, 403
Lead, films, stripping from surface, 12
Lead-antimony alloys: dispersion-hardenable, effect of arsenic, 573
Lee, A. R., Stuart, J. M. and Bengough, G. D.: *Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions*, 29
Lincoln, E. S.: *Discussion on Corrosion of Tin and Its Alloys*, 147
Lyon, A. J.: *Stability of Aluminum and Magnesium Casting Alloys*, 333; *Discussion*, 349

M

Magnesium alloys: binary, heat treatment effect on structure and properties, 309
stability of casting alloys, 333
Mantell, C. L.: *Corrosion of Tin and Its Alloys*, 111; *Discussion*, 146, 148
Matuyama, K.: copper-silicon diagram, 418
McAdam, D. J., Jr.: *Corrosion of Metals as Affected by Stress, Time, and Number of Cycles*, 56; *Discussion*, 54
Discussions: on Diffusion of Zinc into Copper, 556
on Some Aspects of Corrosion-fatigue, 53
McKay, R. J., Fraser, O. B. J. and Searle, H. E.: *Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk*, 175
McKinney, P. E.: *Discussion on High-strength Brasses*, 530
Merica, P. D., Waltenberg, R. G. and Freeman, J. R.: diagram of aluminum end of Al-Mg system, 352
Metallographic Study of Tungsten Carbide Alloys (Gregg and Küttner) 581
Milk: affected by corrosion of containers, 217
flavor affected by metal containers, 212
Monel metal: corrosion. *See* Corrosion of Metals.
Moore, H. F.: *Discussion on Some Aspects of Corrosion-fatigue*, 53
Muntz metal (*See also* 60:40 Brass):
heat-treated, cleavage structure, 498, 505
grain growth, abnormal, 503, 505

N

Nickel: corrosion. *See* Corrosion of Metals
Nickel alloys, acid-resistant, 149

P

Palladium-copper alloys: age-hardening mechanism, 399
Passivity of Metals, and Its Relation to Problems of Corrosion (Evans) 7
Peirce, W. M.: *Discussion on Diffusion of Zinc into Copper*, 558
Peirce, W. M. and Anderson, E. A.: *Some Practical Aspects of Creep in Zinc*, 560
Pennsylvania: Lehigh Valley, corrosion of metals, 280
Pewter: differs from Britannia metal, 373

PHILLIPS, A. J.: *Discussion on Some Observations in Heat Treatment of Muntz Metal*, 505
PILLING, N. B.: *Discussions: on Corrosion of Metals in the Lehigh Valley*, 288
on Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids, 279
on Some New Developments in Acid-resistant Alloys, 158
PILLING, N. B. AND ACKERMAN, D. E.: *Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids*, 248
Platinum-copper alloys: age-hardening mechanism, 399
Porosity: in bronze castings, causes, 479
Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk (MCKAY, FRASER AND SEARLE) 175; *Discussion*, 219
Precious metals (*See also* Names of Metals): alloys, age-hardening mechanism, 399
alloys, effect of heat treatment, 406
PULSIFER, H. B.: *Smoothing and Etching Cupronickel, Bronze, Brass and Steel*, 291; *Discussion*, 308

Q

Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions (BENGOUGH, STUART AND LEE) 29

R

RAWDON, H. S.: *Correlation of Laboratory Corrosion Tests with Service: Weather-exposure Tests of Sheet Duralumin*, 220; *Discussion*, 243
REINHARD, C. E.: *Corrosion of Metals in the Lehigh Valley*, 280; *Discussion*, 290
Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids (BEDWORTH) 160; *Discussion*, 171
Resistance of Iron-nickel-chromium Alloys to Corrosion by Acids (PILLING AND ACKERMAN) 248; *Discussion*, 278
RUDOLFI, E.: copper-silicon diagram, 414, 437, 439

S

ST. JOHN, H. M.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 491, 494
SANFOURCHE, M. A.: copper-silicon diagram, 415, 437, 438, 439
SCHUMACHER, E. E. AND ELLIS, W. C.: *Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys Containing Nickel and Silicon*, 535; *Discussion*, 550
Scrap metal: testing before buying, 492
SEARLE, H. E., FRASER, O. B. J. AND MCKAY, R. J.: *Practical Application of Corrosion Tests: Resistance of Nickel and Monel Metal to Corrosion by Milk*, 175
SELJESATER, K. S.: *Effect of Arsenic on Dispersion-hardenable Lead-antimony Alloys*, 573
Shrinkage, incipient: in bronze castings, 475
in some non-ferrous alloys, 475
Sieverts, A.: law of solubility of gas in metal, 443, 445
Silver alloys: age-hardening mechanism, 399
dispersion hardening, cause and effect, 411
etching reagent, 403, 405
SMITH, C. S.: *Constitution of the Copper-silicon System*, 414; *Discussion*, 441
Discussions: on Equilibrium Relations in Aluminum-magnesium Alloys of High Purity, 368
on Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys, 550
on High-strength Gold Alloys for Jewelry, 405
on Resistance of Copper-rich Copper-silicon-manganese Alloys to Corrosion by Acids, 174
SMITH, H. B. AND EGEBERG, B.: *Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal*, 373; *Discussion*, 383
SMITH, W. S.: *Discussion on Corrosion of Tin and Its Alloys*, 146
Smoothing and Etching Cupronickel, Bronze, Brass and Steel (PULSIFER) 291; *Discussion*, 308
Smoothing and etching cupronickel, bronze, brass and steel, by hand methods, 291
Some Aspects of Corrosion-fatigue (FULLER) 47; *Discussion*, 53
Some New Developments in Acid-resistant Alloys (FIELD) 149; *Discussion*, 158
Some Observations in Heat Treatment of Muntz Metal (VAN WERT) 498; *Discussion*, 505
Some Practical Aspects of Creep in Zinc (PEIRCE AND ANDERSON) 560
SPELLER, F. N.: *Discussions: on Inhibition of Corrosion of Aluminum by Soaps*, 247
on Some Aspects of Corrosion-fatigue and on Corrosion of Metals as Affected by Stress, Time, and Number of Cycles, 53
SPRING, L. W.: *Discussion on Incipient Shrinkage in Some Non-ferrous Alloys*, 492
Stability of Aluminum and Magnesium Casting Alloys (LYON) 333; *Discussion*, 347
Steel: corrosion. *See* Corrosion of Metals.
etching and smoothing by hand methods, 300
STUART, J. M., BENGOUGH, G. D. AND LEE, A. R.: *Quantitative Measurement of Corrosion of Metals in Water and Salt Solutions*, 29

T

Thoran, metallographic study, 583
Tin: chemical properties, 113
corrosion. *See* Corrosion of Metals.
forms and various characteristics, 111

TOWNSEND, J. R.: *Discussion on Heat Treatment and Mechanical Properties of Some Copper-zinc and Copper-tin Alloys*, 549
Treatment and Structure of Magnesium Alloys (GANN) 309
Tungsten carbide alloys: metallographic study, 581

V

VAN WERT, L. R.: *Some Observations in Heat Treatment of Muntz Metal*, 498

W

Walramite, metallographic study, 583
WEIGAND, S. A. AND BOLTON, J. W.: *Incipient Shrinkage in Some Non-ferrous Alloys*, 475
Widia, metallographic study, 583
WISE, E. M.: *High-strength Gold Alloys for Jewelry and Age-hardening Phenomena in Gold Alloys*, 384; *Discussion*, 403 et seq.
WITHERELL, C. S.: *Discussion on Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal*, 381
WRIGHT, T. A.: *Discussion on High-strength Gold Alloys for Jewelry*, 403

Z

Zinc: corrosion. *See* Corrosion of Metals.
diffusion into copper, rate and temperature, 552
roof sections, creep tests, 560
roof sections, laboratory loading tests, 560
safe maximum fiber stress, 565